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SUSTAINABLE SYNTHETIC FUELS FROM WASTE BIOMASS FOR THE TRANSPORT INDUSTRY

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This thesis set out to investigate the sustainability of synthetic fuel obtained from waste biomass. There were many emerging alternative transportation fuels, which could reduce the world's reliance on fossil fuels; however, there are particular concerns about the techno-socio-economic viability of synthetic fuels. Moreover, there were many different technological options for the production of these synthetic fuels, each with their own multifarious challenges and benefits. Following a review of thermochemical conversion technologies and fuel quality upgrading processes, six alternative synthetic fuel production scenarios were established as the most promising options to pursue. The six synthetic fuel production scenarios investigated utilised fast pyrolysis of corn stover in a fluidised bed reactor to produce bio-fuel. The fuel upgrading stages considered comprised of single-stage and two-stage hydrotreating, esterification, ketonisation and hydrocracking. Life Cycle Assessment (LCA) was adopted to examine the environmental feasibility of these scenarios in comparison to conventional diesel fuel, and an economic analysis was performed to determine the sensitivity of several key financial indicators. The expected CO_2 equivalent emissions from synthetic fuel production were found to be between 2240 and 6000 gCO_{2e}/kg of synthetic fuel and the use of it will emit 3200 gCO_{2e}/kg, which was greater than the emissions arising from the production of diesel fuel (approximately 4200 gCO_{2e}/kg of diesel fuel); net expected emissions including CO_2 absorption and fuel combustion in a well-to-wheel analysis were also evaluated and indicated that the emissions could be as low as -926 gCO_{2e}/kg of synthetic fuel. The expected cost of synthetic fuel was found to range from \$1.42 to \$10.94 /kg and was reduced in the most optimistic case to between \$0.64 to \$4.34 /kg of synthetic fuel. To perform a systematic comparison of the six scenarios, the thesis went on to use the Analytic Hierarchy Process (AHP) and The Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS): multi-criteria decision analysis methods. A recommendation arising from the AHP and TOPSIS analysis was that if the system was optimised, esterification and esterification-ketonisation with single-stage hydrotreating could provide reasonable trade-offs between product quality, cost and achievable environmental gains.

Keywords: synthetic fuel; pyrolysis; life cycle assessment; bioenergy; AHP; TOPSIS; multi-criteria decision analysis

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Nomenclature:

A - decision matrix consisting of *m* alternatives and *n* criteria

A_b - positive ideal solution

ADP - abiotic depletion potential

AHP - analytic hierarchy process

$α_{ij}$ - the intersection of each alternative and criteria (numerical judgments of matrix A)

AP - acidification potential

atm - atmosphere, standard unit of pressure

A_w - Negative ideal solution

BEVs - battery-electric vehicles

BN - number of kilograms needed to obtain one kilogram of synthetic fuel

BP - biomass processed, the number of kilograms processed every day

BTL - biomass to liquid

Cc - capital cost

CCbm - capital cost per kg biomass

CCd - capital cost per day

CCdbf - capital cost per day, per kg biofuel

CCbf - capital cost per kg biofuel

CCy - capital cost per year

CH_4 - methane

CI - consistency index

Co - cobalt

CO - carbon monoxide

CO_2 - carbon dioxide

CR - consistency ratio

CW - compromised weightings

DCB - dichlorobenzene

DFy - debt financing (in years), the period of time to pay back the debt

d_{ib} - L2-norm (Euclidian) distances from the target alternative *i* to the best a conditions

d_{iw} - L2-norm (Euclidian) distances from the target alternative *i* to the worst conditions

E_j - entropy value j^{th} criteria

ELECTRE - Elimination et choice translating reality

Ent. - entropy

EP - eutrophication potential

eq. - equivalent

EW - entropy weightings

Exp - expected

FCC - Fluid catalytic cracking

FCEVs - fuel-cell electric vehicles

FCI - Fixed capital includes

Fe - Iron

FT - Fischer-Tropsch

FTS - the Fischer-Tropsch synthesis

GHGs - greenhouse gases

GWP - global warming potential

H - Hydrogen

IC - indirect costs

IRB - interest rate of debt financing

IRR - internal rate of return, the possible profit of the company

ITR - income tax rate, imposed by the federal government

HANP - Hierarchical Analytical Network Process

HDO - hydrodeoxygenation

HEVs - hybrid electric vehicles

HK - hydrocracking

HT - hydrotreating

K - Potassium

K_2O - potassium oxide

LCA - life cycle assessment

LHV - lower heating value

MAE - microwave assisted extraction

MC - material cost

MCbf - material cost per kg

MCDM - multi-criteria decision-making

MFSP - minimum fuel product selling price

Min - minimum

Mo - molybdenum

MQ - material quantity

MSP - minimum selling price

MSW - municipal solid wastes

MTG - methanol to gasoline process

n - the size of the matrix

N - Nitrogen

NCG - pyrolysis non-condensable gases

Ni - nickel

N_2O - nitrous oxide (dinitrogen monoxide)

NPV - net present value

O - Oxygen

Oc - operational cost

OCbf - Operational cost per kilogram of synthetic fuel

P - Phosphorous

Pc - Process cost

Pd - palladium

pH - a logarithmic scale used to specify the acidity or basicity of an aqueous solution

PHEVs - plug-in hybrid electric vehicles

PO_4^{3-} - phosphate

P_2O_5 - phosphorus pentoxide

ppm - parts per million

PROMETHEE - Preference ranking organization method for enrichment evaluation

PSE - pressurised solvent extraction

Pt - platinum

R - normalised matrix (A)

RI - consistency index

r_{ij} - the data of the ith evaluating object on the criteria

Ru - ruthenium

SF - on stream factor, operating period of time

SFE - supercritical fluid extractor

S - Sulfur

SO_2 - sulfur dioxide

TC - total cost

Tcc - total capital cost

TDIC - total direct and indirect costs

TIC - total installed cost

t_{ij} - weighted normalised value

TOPSIS - technique for order of preference by similarity to ideal solution

UE - ultrasound extraction

ULEV - ultra-low emission vehicles

UOP - universal oil products

W - the principal eigenvector of the matrix A

WCC - working capital cost (including land) – maintaining daily operation & short-term debt

WGS - water-gas shift

w_j - weight of jth criteria

WPM - weighted product method

WSM - weighted sum method

α_j - pair-wise weightings

β_j - entropy weightings

λ_{max} - lambda-max, the principal eigenvalue of matrix A

Organisations nomenclature:

AIRS - Athmoshperic Infrared Sounder

EBRI - European Bioenergy Research Institute

EPA - Environmental Protection Agency

GOV.UK - United Kingdom public sector information website

IEA - International Energy Agency

IPCC - Intergovernmental Panel on Climate Change

ISO - International Organization for Standardization

LowCVP - The Low Carbon Vehicle Partnership

NASA - National Aeronautics and Space Administration

NOAA - National Oceanic and Atmospheric Administration

REN21 - Renewable Energy Policy Network for the 21st Century

RETD - Renewable Energy Technology Deployment

RTFO - Renewable Transport Fuel Obligation

SMMT - Society of Motor Manufacturers & Traders

SPC - Shortsea Promotion Centre

UNFCCC - United Nation Framework Convention on Climate Change

UNIDO - United Nations Industrial Development Organization

Chapter 1

1. Introduction

This opening chapter provides an overview of the current situation regarding climate change and the impact of alternative fuels particularly on the transportation sector. The current problems and challenges associated with alternative fuels are established and the aims and objectives of the thesis are outlined.

1.1. Overview of global situation

1.1.1. The effect of increasing CO_2 levels

The drastic increase in the emissions of carbon dioxide (CO_2) within the last 60 years from using fossil fuels is widely believed to be the major cause of increasing global temperatures (SPC Finland, 2012; Committee on Climate Change, 2018). In 1960 the carbon dioxide level was 317 parts per million (ppm); and by 2015 it had increased to over 400 ppm - a first in human history (NOAA Research, 2018). As CO_2 levels are increasing every year, Global Warming has become a more serious issue. Recent global CO_2 levels were reported to be as high as 403.52 ppm in November 2016 and 405.58 ppm in November 2017. The CO_2 levels observed at Mauna Lao are comparable to Global average marine surface annual mean data (NOAA Research, 2018), validating the fact that rising CO_2 emissions is a global issue. Figure 1.1 shows the annual average temperature (measured over both land and oceans). Red and blue bars indicate the temperatures below and above the average temperature respectively since 1901 to 2000 (approximately $57.6^oF \sim 14.2^oC$). The black line indicates the atmospheric CO_2 concentration and it is measured in ppm. Whilst a long-term global warming trend can be identified, the temperatures are fluctuating each year (U.S. Global Change Research Program, 2009).
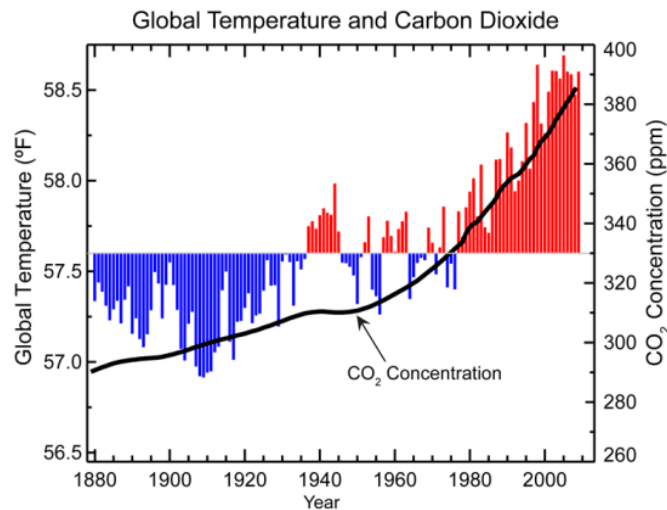
Figure 1.1: Global annual average temperature vs CO_2 concentration (U.S. Global Change Research Program, 2009)

If the CO_2 emissions continue to rise at the same rate, values as high as 963ppm could be reached by 2100, which have been estimated to result in a temperature increase of up to 3.7°C by the next century (Anderson, Hawkins and Jones, 2016).

1.1.2. Climate change due to greenhouse gases

The gases that trap heat in the atmosphere are known as greenhouse gases. The greenhouse effect is a result of the radioactive imbalance between the sun's radiation in the atmosphere and the absorption of re-emitted infrared radiation. The greenhouse gas effect is a natural phenomenon that keeps temperatures suitable for life and it is powered by solar radiation. Due to the atmosphere's transparency, the sun's radiation reaches the planet's surface. The Earth and the atmosphere reflect some of the radiation, but most of it is absorbed by the earth's surface, resulting in infrared radiation emissions. Some infrared radiation passes through the atmosphere, but the rest is trapped due to the greenhouse gases and this results in heating of the Earth's surface (Online Sciences, 2014; Anderson *et al.*, 2016; Oxford University Press, 2018).

Releasing carbon dioxide into the atmosphere increases the greenhouse effect and causes further global warming. By comparing Mid-Troposhperic CO_2 levels provided by NASA AIRS (Athmoshperic Infrared Sounder) data, it can be noticed that the CO_2 levels increased visibly between July 2003 and April 2013, see Figure 1.2. A significant change can be seen in the CO_2 levels, especially near the north pole.
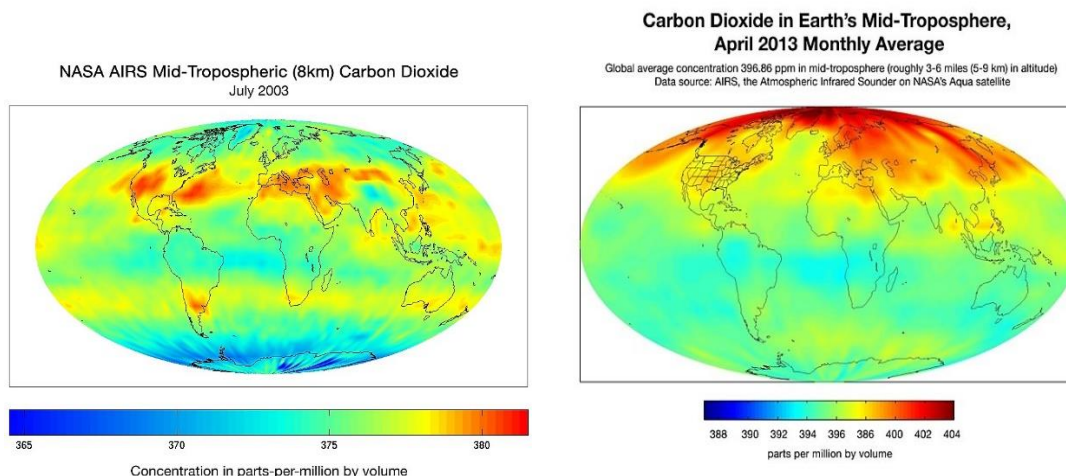
Figure 1.2: NASA AIRS Mid-Troposhperic CO_2 levels for July 2003 (NASA AIRS, 2008) and April 2013 (NASA AIRS, 2013). Dark blue corresponds with lower concentrations of CO_2 and red shows higher concentrations of CO_2

The world is not warming uniformly and air temperatures have increased at a faster rate on the land, in comparison to the oceans. In comparison to the recorded average surface temperatures between 1986 - 2005, Figure 1.3 shows a projection of the expected increases in temperature between 2080 - 2100 (The Royal Society and National Academy of Sciences, 2014). The Royal Society (The President, Council and Fellows of the Royal Society of London for Improving Natural Knowledge) is the oldest national scientific institution in the world and fulfills a number of roles as: promoting science and its benefits, supporting outstanding science, fostering international and global co-operation, education and public engagement. The National Academy of Sciences is a United States nonprofit, non-governmental organization where members are elected based on their distinguished and continuing achievements in original research and serve pro bono as 'advisers to the nation'. Their scientists have considered various facts and uncertainties, and are very confident that if emissions continue the present trajectory, warming of 2.6 to 4.8 °C would be expected by the end of the 21st century. It can be seen that there is a correlation with the higher CO_2 levels giving rise to a higher increase in the temperature in the high northern latitudes. The highest increase in temperature is predicted to take place over the Artic due to snow and ice loss resulting in less radiation being reflected from the surface area (Britannica Educational Publishing, 2011).
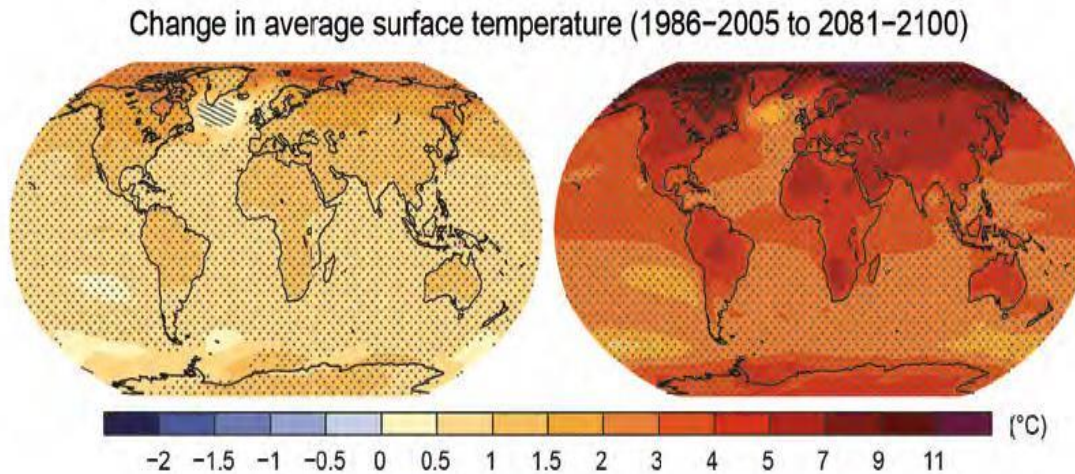
Figure 1.3: Global warming projections over the 21st century (The Royal Society and National Academy of Sciences, 2014)

1.1.3. Anthropogenic impact on greenhouse gas emissions

CO_2 is the main greenhouse gas in the atmosphere making up approximately 80% of the total greenhouse gases emissions (IPCC, 2015; EPA, 2017a). Burning fossil fuels, solid waste and wood products produce the majority of CO_2 emissions. Other greenhouse gases are Methane (CH_4) that is emitted in production of coal, natural gas and oil, as well as during organic waste decay in landfills; Nitrous oxide (N_2O) emitted in industrial activities and during fossil fuels combustion; and Fluorinated gases (F-gases) are emitted during a range of industrial processes (EPA, 2017a). Figure 1.4 shows the greenhouse gas emissions by gas (IPCC, 2015; EPA, 2017a). Since greenhouse gases are considered to be responsible for global warming (Anderson *et al.*, 2016), a global warming potential can be calculated for each greenhouse gas based on how long it remains in the atmosphere and how strongly it absorbs the energy (EPA, 2017a).
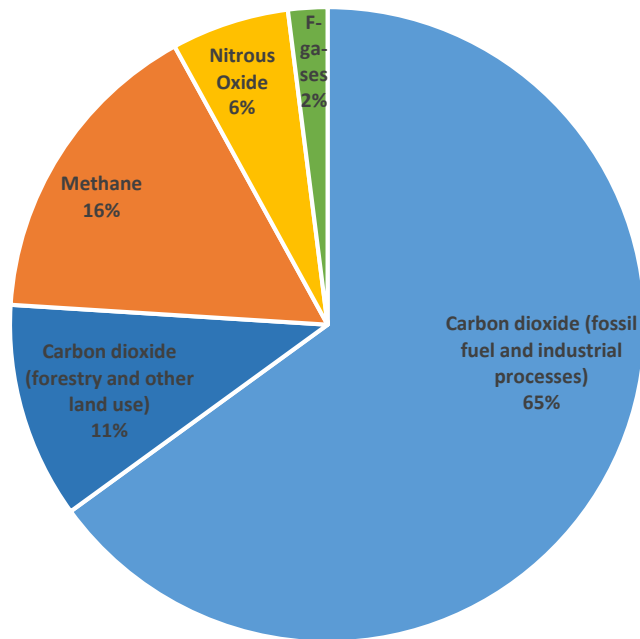
Figure 1.4: The greenhouse gas emission by gas (IPCC, 2015; EPA, 2017a)

Globally, from the total human-induced CO_2 emissions, approximately 82 % are the result of burning fossil fuels and the rest from deforestation. The charts in Figure 1.5 shows the percentage of each sector that uses fossil fuels. The main source of human-produced CO_2 emissions is coal-burning power plants. A share of 21% from the total human-induced CO_2 emissions are produced by the transport industry (Britannica Educational Publishing, 2011), but values of over 28% have also been reported in US (EPA, 2017b), bringing the transportation industry on the same levels as electricity generation. In order to reduce carbon dioxide levels, renewable alternatives to fossil fuels are needed.
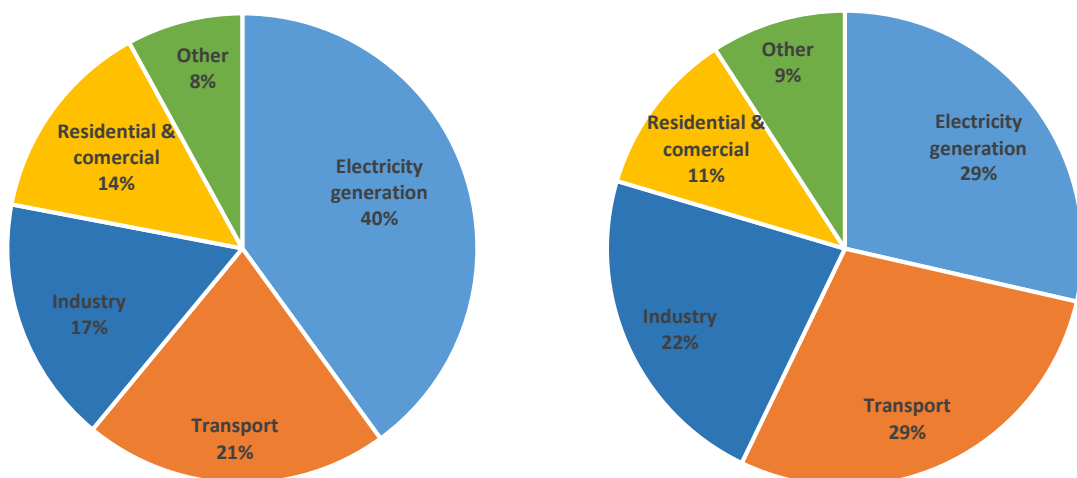
(a) (Britannica Educational Publishing, 2011)   (b) (EPA, 2017b)

Figure 1.5: Human induced CO_2 from fossil fuels – by sector, globally (a) & in US (b)

1.1.4. Climate change effects

Global warming is considered to be responsible for a range of climate change effects. Changes in precipitation patterns can lead to extreme weather conditions such as downpours and a decrease of summer precipitations, which is predicted to increase droughts. Other global warming effects include increased atmosphere moisture and oceans heat content, polar ice-melt resulting in increasing sea-levels, and tropical cyclones (including hurricanes and typhoons). It is expected that there will be both positive and negative outcomes of climate change as although in some parts of the world agriculture will be enhanced due to earlier spring weather, in other areas the frequency of droughts or floods could increase (Britannica Educational Publishing, 2011; The Royal Society and National Academy of Sciences, 2014). Enhanced forestry growth has been posited as a potential remedy in previous research (Buitenwerf *et al.*, 2012; Cha *et al.*, 2017), but the positive effect has been offset by forest fires or beetle infestations caused by warmer weather.

1.1.5. The fossil fuel problem

Along with climate change concerns, the global demand for energy is rapidly increasing and fossil fuels reserves are decreasing – as crude oil is exploited at a much faster rate than its natural regeneration (Cherubini and Strømman, 2011). Hence, there is significant interest in finding alternative sources of energy.

Most of the energy that fuels our lives comes from plants; either fossil fuels that formed in the prehistoric period or food that we eat. By burning fossil fuels that have formed over hundreds of millions of years by fossilization of the plant remains, the carbon that was previously locked is released into the atmosphere, warming it and potentially producing devastating consequences.

1.1.6. The need for cleaner transportation fuels

The transport sector is currently the fastest growing energy consumer and producer of greenhouse gases (Eurostat, 2015), and transport globalisation also raises concerns regarding CO_2 and other greenhouse gases emissions. The main international transport activities are: shipping, aviation, road and rail. Increasing globalisation had led to international shipping and air-transport development. As a result, measures have to be taken to reduce greenhouse emissions produced by all transport activities. Strategies to

reduce the environmental impact caused by the transport industry require government intervention in the form of changes to the regulatory policy. This is complex even within individual countries, and even more complicated when considering international expansions (Braathens, 2010).

Between 1925 and 2002, shipping CO_2 emissions more than doubled, and SO_2 (sulfur dioxide) emissions more than tripled, (Endresen *et al.*, 2007) – currently they are responsible for 2 - 4% and 4 - 9% of total global anthropogenic emissions respectively. By 2020 maritime fuel consumption and emissions may be increased by 30% and by 2050 the maritime CO_2 emissions can reach between 200 - 300% of current values (Eyring *et al.*, 2005). Due to the expected increase in maritime transport it is expected that there will be a significant increase in emissions from the shipping sector, new regulations and other policy measures may be needed to control the CO_2 emissions and limit the fossil fuel sulphur content that lead to deposition in nearby coastal regions (Braathens, 2010). The aviation industry generates approximately 2% of the world's CO_2 emissions (Chiaramonti *et al.*, 2014), but because of the fast growth rate it is expected to increase by 70% by 2020 and by 300 - 700% by 2050 (European Commission, 2018b). Road transport contributes approximately 20% of the total European CO_2 emissions, 15% produced by light-duty vehicles and 6% by heavy-duty vehicles. EU legislation require that vehicle CO_2 emissions to be reduced by 10% by 2020 (European Commission, 2018a).

Concerns about emissions from different sectors has led to global acts being made to mitigate and reduce further climate change. The United Nation Framework Convention on Climate Change (UNFCCC) was created in 1992 and its aim was to stabilise greenhouse gases in the atmosphere. In 1997, the Kyoto Protocol set targets for 37 industrialised countries for the period 2008 - 2012. Targets were met and greenhouse gas emissions were reduced globally by over 10%. However, this was not enough. A second Kyoto Protocol was agreed for the period from 2013 to 2020, and the UK and EU are part of the participating counties. Further to this, the Paris Agreement set out in December 2015, was the first truly global agreement to reduce emissions by 2030 (SPC Finland, 2012; Committee on Climate Change, 2018).

As the transportation industry contributes a significant amount to the total human-induced CO_2 emissions, the UK government aims to reduce greenhouse gas emissions

by investing in low-carbon energy sources, increasing energy efficiency and improving fuel standards for the transportation industry (GOV.UK, 2018). The Europe 2020 strategy has set some goals, such as greenhouse gas (GHG) reduction of 20% by 2020 compared to 1990, and to increase the use of renewable energy to 20% of the total consumption of energy. In the field of transport, Transport White Paper 2011 includes the aims of Europe 2020 and extends its goals by 2050. The White Paper transport strategy goals are to increase mobility and reduce emissions. As EU transport relies on oil and oil products about 94 - 96% of its total energy needs, Transport White Paper 2011 requires GHGs reduction from the transportation sector (SPC Finland, 2012; IEA, 2012). More specifically, in November 2017 the European Commission proposed new CO_2 standards for passenger cars and light commercial vehicles in the EU for the period 2020 onwards (European Commission, 2018a).

1.1.7. Alternative sources of energy for the transportation industry

The transition from conventional fuels to renewable energy sources in transport is essential for reaching climate change targets. Moreover, the diversification of energy sources within the transportation sector could also increase energy security. There are two main technologies pathways: transport electrification and biofuels.

Transport electrification consists of ultra-low emission vehicles (ULEV) that release extremely low CO_2 emissions compared to conventional transportation fuels. There are four main type of ULEV and their key characteristics are summarised below (IEA-RETD, 2015; NREL, 2015; Energy and Climate Change Committee, 2016): Battery-electric vehicle (BEVs) are vehicles that run only on electricity and have to be plugged into a grid for recharging; Plug-in hybrid electric vehicles (PHEVs) can also be recharged by plugging into the grid, but are able to switch between electricity and fossil fuels; Hybrid electric vehicles (HEVs) can switch between electricity and fossil fuels, but are equipped with smaller batteries that charge while driving; and Fuel-cell electric vehicle (FCEVs), which use hydrogen to power an electric motor. The vehicle technology (Fuel Cell Electric Vehicles) and the required energy infrastructure are completely different in comparison to internal combustion vehicles.

Biofuels are a promising option, which are already widely used. They can be used in the same way as conventional fuels and distributed via existing infrastructure. Some biofuels do require certain adjustments in vehicles and infrastructure, but compared to

hydrogen and electric vehicles in particular, the fuel can be considered to require less radical change to implement as the required vehicle technology is already mature and the vehicle performance and usage is similar to those of internal combustion vehicles (IEA-RETD, 2015). Whilst energy can be provided through several forms of renewable alternatives (sun, wind, biomass, etc.), biofuels can act as a direct replacement to gasoline/petrol and diesel. Moreover, they are currently the only viable alternative to fossil fuel resources for the production of commercial aviation fuels and chemicals.

Currently, most of the total energy demand for transport is provided by oil, 3% by natural gas and other fuels, 2% by biofuels and 1% by electricity (IEA, 2012). Therefore, key policies such as the Renewable Transport Fuel Obligation (RTFO) – which is one of the most important UK Government's non-electricity decarbonisation policies – must be implemented to meet the 2020 targets for transport (set to 10%). Unfortunately, RTFO stopped at 4.75%, therefore further incentives are still needed (Energy and Climate Change Committee, 2016).

1.1.8. First and second generation transportation biofuels

Approximately 5% of the global transportation demand is met by biofuels (IEA, 2011), and biomass is set to play an increasingly important role in reducing transport related CO_2 emissions. Currently, the majority of biofuels used for transportation are derived from food crops; this has raised fears of increasing food prices and causing food shortages. There are also concerns with the environmental impacts of using large quantities of fertilisers and pesticides to cultivate certain energy crops (IEA, 2011).

Bioenergy is commonly used for renewable natural materials - as plants or animal waste - used to produce electricity, heat and transport fuels. It is usually called biomass when solid, biofuel when liquid and biogas when gaseous. There is a variety of ways to convert biomass into a liquid biofuel, and these liquids are often classified as either first or second - generation fuels. 'First-generation biofuels' are derived from sources of starch, sugar, plant oils and animal fats, and the most commercialised fuels are bioethanol and biodiesel. 'Second-generation biofuels' are produced from lignocellulosic biomass such as woody crops, agricultural residues and other waste feedstocks and, unlike fuels from edible food stuffs, do not require agricultural land, thus alleviating concerns about the potential for food shortages. Biogas is produced by anaerobic digestion (AD) of plant matter, and includes biomethane – which is a

component of landfill gas or biogas that forms when organic waste decomposes in landfills or in special containers (digesters). All these forms of bioenergy account for approximately 71% of the UK's renewable energy through electricity, heat and transport (Naik *et al.*, 2010; Energy and Climate Change Committee, 2016).

Biofuels contain carbon which, when burnt, generate mostly water vapour and carbon dioxide, but due to their lifespan CO_2 absorption (through photosynthesis) they can provide beneficial environmental gains. A drawback of first-generation biofuels, presently used for the transportation industry, is that they are derived from food crops or crops that require vast expanses of land. On the other hand, first-generation biofuel production technology is well-established. For example, E10 is a fuel consisting of around 10% ethanol – hence called the E10. E10 is a governmental measure to meet the emissions targets, and therefore all the cars manufactured post 2011 must be compatible to it. The Society of Motor Manufacturers & Traders (SMMT) exists to support and promote the interests of the UK automotive industry at home and abroad. They estimate that 92% of the UK petrol-engine vehicles are compatible with E10. This is projected to reduce greenhouse gas emission of petrol-vehicles by over 6%. Moreover, Brazil is mixing fuels with 28% ethanol (LowCVP, 2017; RAC, 2018). As the UK has committed to 80% GHG reduction by 2050 (LowCVP, 2017) concerns were raised on the 'crop-cap' governmental measure that set a limit of 1.5% for transport biofuels. The RTFO commitment will need to be increased with an appropriate crop cap (LowCVP, 2017; RAC, 2018); however, European Commissions (2017) has already included an increase in the 'cap' for first-generation fuels to 7%, through the Renewable Energy Directive for 2030 (REN21, 2018).

Because of the potential stress that their production places on land displacement and food commodities, first-generation biofuels may be less suitable than second-generation biofuels. Second-generation biofuels can be obtained from fast growing non-food crops, agricultural residues, grasses and other waste feedstock, and they are generally considered more sustainable and environmentally friendly (Cherubini and Strømman, 2011; Jahirul *et al.*, 2012). In contrast, the conversion to high quality biofuels that can be used in transportation vehicles and can compete with fossil fuels requires more complex and energy intensive conversion processes (Naik *et al.*, 2010). Whilst a significant amount of research has been carried out on the use of first-generation

biofuels for transportation, research on producing sustainable transportation fuels from second-generation biofuels is more limited.

Biodiesel can be produced directly from vegetable oil (palm oil, soybean oil, rapeseed oil, castor seed oil), animal oil and fats; tallow and waste cooking oil, which can be converted by transesterification (Meher, Sagar and Naik, 2006). Whereas synthetic fuel can be obtained by biomass pyrolysis or gasification with Fisher Tropsch (FT) processing, which can be used to convert gas into a liquid fuel (Trippe *et al.*, 2011). For converting waste biomass into a second-generation biofuel, a range of biochemical and thermochemical processes can be used. The thermochemical conversion methods include pyrolysis, liquefaction and gasification, and products from these processes require significant amounts of upgrading to improve their quality to meet appropriate fuel specifications. Pyrolysis involves the thermal degradation of organic matter in the absence of oxygen to produce bio-oils, non-condensable gases and a solid char residue. It has gathered much interest as a promising option for producing synthetic transportation fuels (Iribarren, Peters and Dufour, 2012; Wright *et al.*, 2010b). However, the technology still requires significant research and development before commercialisation. Although there has been a significant number of studies investigating the thermochemical process for converting waste biomass into bio-oil via pyrolysis, there is a very limited amount of research into the upgrading pathway of pyrolysis bio-oils into viable transportation fuels. Highly oxygenated, unstable and acidic bio-oils (Oasmaa and Meier, 2005) have to be improved before they can be used as transportation fuels (Bridgwater, 2012a; Bridgwater, 2012b). 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 and techno-economical compatibility in comparison to conventional fossil fuels. A third generation biofuel has also been considered, referring to fuels derived from algae (Dragone *et al.*, 2010).

Keeping track of biofuel policies is challenging, as legislation is frequently modified by numerous countries. Because of this the Renewable Energy Policy Network for the 21st Century (REN 21), a global energy policy network, was established. REN21 reported that the number of countries with renewable energy targets increased to 165 in early 2015, among which 164 countries had renewable energy targets, and an estimated 145 countries had renewable energy support policies in place (REN21, 2015). The US

provides funds in the form of grants and loans for cellulosic biofuels R&D (research and development), and for development and construction of advanced biorefineries. The EU also offers additional benefits for second-generation biofuels as compared to conventional fuels (Carriquiry, Du and Timilsina, 2011); and has already started to include biofuel policies to comprise specific requirements for the use of next-generation cellulosic biofuels. In the Renewable Energy Directive for 2030, European Commission (2017) recommended a target of 3% for advanced biofuels (REN21, 2018).

After 2020, transport is expected to depend on a combination of bioenergy and electrification. At the moment, the UK government cannot rely on electrification alone, due to limited electricity-network capacity. Therefore, further studies are needed to analyse the sustainability, and therefore the risk and benefits, of the transportation fuels produced from renewable materials through different technologies (Energy and Climate Change Committee, 2016). Whilst there has been lots of research on first-generation fuels, there is not as much on the sustainability of second-generation fuel. Second-generation or 'advanced' biofuels could provide significant carbon savings without concerns about crop sustainability and also can offer an economic opportunity with a real potential to develop an internal industry that contributes to economic growth and highly skilled jobs in a global market (RTFO, 2016). The limited potential of first-generation biofuels to replace fossil fuels (due to sustainability concerns) and reduce greenhouse gas emissions requires an urgent transition to second-generation biofuels. The main challenges faced by second-generation biofuels are of technological and economical natures. Therefore, political interventions could accelerate the transition to second-generation biofuels by adapting policies to support the R&D of advanced biofuels and discouraging the production of fossil fuel-based transportation fuels. In addition, policies to reduce the cost of biofuel production are needed (Carriquiry *et al.*, 2011).

1.1.9. Biomass to bio and synthetic fuels potential

Biomass is one of the main sources of energy worldwide. Yet, there are various types of biomass which have different potential benefits and characteristics and it is hard to describe biomass feedstock as a whole (Demirbas, 2009). Therefore, biomass can be divided into the following main categories (Demirbas, 2009; EESI, 2018):

- Grains and starch crops: sugar cane, corn, wheat, sugar beets, sorghum, industrial sweet potatoes, etc.

- Agricultural residues: corn stover, wheat straw, rice straw, orchard prunings, etc.

- Forest products: wood, logging residues, trees, shrubs and wood residues, sawdust, bark, etc.

- Energy crops: short-rotation woody crops, herbaceous woody crops, grasses, starch crops, sugar crops, forage crops, oilseed crops, switchgrass, miscanthus

- Aquatic plants: algae, water weed, water hyacinth, reed and rushes

- Animal by-products: tallow, fish oil, manure, etc.

- Urban and suburban wastes: municipal solid wastes (MSW), lawn and urban wood wastes, hazardous waste, non-hazardous waste, inert waste, liquid waste, industrial organic wastes, municipal sewage and sludges

Biomass is an abundant, widespread and relatively cheaply available source of energy, and accounts for about 14% of global energy demand (World Energy Council, 2016), but it is mainly used in traditional, inefficient applications in developing countries. In the majority of countries, the generation of biomass is quite high, resulting in vast quantities of waste (e.g. agricultural, industrial and municipal waste). Much of this waste accumulates, creating problems regarding their disposal, such as burning which leads to serious environmental issues. Therefore, converting waste into liquid fuel should be considered (Hossain, Hasan and Islam, 2014). Părpăriţă *et al.* (2014) believed that replacing fossil fuels with wood fuels could reduce net CO_2 atmospheric emissions by over 90%. This would be beneficial for the environment, as the emissions of greenhouse gases arising from fossil fuel combustion are perturbing the Earth's Climate (Forster *et al.*, 2007). However, in order to prevent deforestation, waste biomass is considered a more sustainable option.

Biomass is constituted by a large variety of plant species, with varying chemical composition and morphology. Biomass can be divided into five main components: cellulose, hemicellulose, lignin, lipids and starch. The first three constituents are by far the most abundant, and – as they can be gathered from waste streams or directly harvested from biomass stands or forests – their price was found to be lower than other biomass sources, which may require a dedicated agricultural plot (Cherubini and Strømman, 2011). Also, woody materials were found to be preferable compared to food

crops, as they contain much more energy, and lower amounts of pesticides and fertilization materials (Van der Stelt *et al.*, 2011). Due to various molecular structures, cellulose, hemicellulose and lignin decompose differently according to temperature, heating rate and contaminants presence (Yaman, 2004). All living matter on the planet (including materials resulting from animal waste or manure and plants) consists of biomass. The chemical components of biomass are hydrogen, carbon, nitrogen, oxygen, and traces of inorganic species (Goyal, Seal and Saxena, 2008).

Lignocellulosic feedstocks have different advantages and disadvantages and the main ones are included in Table 1.1.

Table 1.1: Advantages and disadvantages of lignocellulosic feedstock (Carriquiry et al., 2011)

Lignocellulosic feedstock	Advantages	Disadvantages
Agricultural residues	Have minimal direct impact on food price Avoid GHG emissions associated with direct and indirect land use changes New source of revenue for farmers	Excess removal will have adverse impacts on soil, crop production and the environment Needs specially designed harvest equipment and storage system
Forest residues	Large amounts available and widely used sources Removal of excess woody material improves forest health and productivity	Limited accessibility Potential reduction of recoverability in harvest areas Competes with current uses

Taking into account the present renewable energy development, as well as the declining petroleum natural sources, waste biomass is considered a more environmental-friendly alternative compared with fossil fuels, reducing GHG emissions, possibly reducing NOx and SOx, and also offering a promising economic potential in the event that fossil fuels prices will increase in the future.

The present study refers to bio and synthetic fuels obtained from waste biomass (lignocellulosic biomass) due to its advantages: available globally, does not have to

compete with food, land or water resources, and reduces landfill. There are also some challenges in the use of biomass; some biomass as food crops or grasses are seasonal, the storage is difficult because of degradation, dust and fire or health hazards. In addition, a big challenge is to find a sustainable way to convert waste biomass to synthetic fuels, because of the structural and compositional complexity.

The biofuels (e.g. ethanol, biodiesel) are derived directly from living matter, while the synthetic fuels include any fuels (produced from coal, natural gas or biomass feedstocks) obtained through chemical conversion (U.S. Energy Information Administration, 2006). Because most of the previous studies in the field refer to the fuels obtained by thermo-chemical conversion of biomass as cellulosic biofuels, hydrocarbon biofuels or just biofuels, this study uses all terms concurrently; however, the term synthetic fuels is used when referring to bio-fuels upgraded from hydro processing techniques.

Research on synthetic fuels must establish the best environmental practices and methods to produce sustainable fuels at a reduced cost. Significant research was carried out on exploring the thermochemical reactor designs and the bio-oil quality and yields achieved. It has also been confirmed that different bio-oil upgrading technologies can lead to commercially viable alternative fuels with similar performance characteristics to transportation fuels. However, more research is required to establish whether upgrading bio-oil to transportation synthetic fuels can be sustainably achieved.

1.2. Aim and Objectives

The project aims to analyse the sustainable production of synthetic fuels from waste biomass for the transport industry. An alternative fuel should offer environmental benefits and decreased dependence on fossil fuels. Advanced biofuels are currently being considered to make the transport industry greener and achieve carbon reduction targets. One emerging option being pursued is synthetic fuels produced from waste biomass using thermochemical conversion and hydroprocessing upgrading methods.

The key research questions that arise on the use of synthetic fuels for the transportation industry are:

Q1 - Can synthetic transportation fuels be sustainable in comparison to conventional fossil fuels?

Q2 - How can existing thermochemical conversion methods for producing synthetic fuels be more sustainable?

Q3 - Are there environmental benefits in comparison to fossil fuel?

Q4 - How expensive are synthetic fuels likely to be in comparison to fossil fuels?

Q5 - How can a trade-off among quality, cost and environmental impact be made among options for producing synthetics fuels?

To address these questions, research on synthetic fuels must establish good environmental practices and methods to produce fuels at a feasible cost. This can be achieved by exploring the thermochemical upgrading processes and by examining the fuel sustainability.

In order to answer these questions, the project has the following specific objectives:

1. Identify promising options for thermochemical conversion of waste biomass into a synthetic fuel.

2. Evaluate the environmental impacts of different processes for producing alternative synthetic fuels in comparison to conventional transportation fuels.

3. Assess the techno-economic feasibility of the different processes for producing synthetic fuels for transport industry.

4. Design a multi-criteria system to assess the feasibility of different processes for producing synthetic fuels.

To meet these objectives and achieve the aim of the thesis, the project was divided into the following sections, each one consisting of several main tasks:

1. Establish alternative scenarios for converting biomass into a synthetic transportation biofuel

      1.1. Review different types of biomass to convert to synthetic fuels

      1.2. Review different types of reactors to convert biomass to bio-oil

      1.3. Review different upgrading methods of bio-oil to synthetic fuels

2. Based on the different conversion technologies, recommend the most promising scenarios to upgrade bio-oil to synthetic fuels

    2.1. Investigate both existing and new concepts based on selected thermochemical upgrading technology

    2.2. Propose improved designs for upgrading pyrolysis bio-oil

3. Evaluate the feasibility of obtaining sustainable synthetic fuel from waste biomass

    3.1. Perform an environmental impact analysis of the different pathways to produce synthetic fuels

    3.2. Implement a financial study for the chosen pathways to produce synthetic fuels

    3.3. Investigate the most sustainable option (using the environmental, financial and technical criteria of different pathways to produce synthetic fuels) by performing multi-criteria decision-making analyses

1.3. Structure of the thesis

The first chapter has given a broad overview of CO_2 levels and other GHG emissions, climate change, alternative sources of energy for transportation fuels, first and second - generation biofuels, and biomass types, conversion methods and policies for transportation biofuels. The potential of second-generation biofuels has also been outlined. The chapter has concluded with the overall aim and objectives for this thesis on sustainable methods to convert waste biomass to synthetic fuels. The subsequent chapters of this thesis are organised as follows:

Chapter 2: A literature review provides wider context on the existing body of knowledge in the research field of synthetic fuels and thermochemical conversion technologies. An exhaustive literature review on biomass feedstocks, thermochemical conversion and pyrolysis reactors, and different bio-oil to synthetic fuel upgrading technologies involved (with advantages and disadvantages) was carried out. The literature review was used to outline a number of promising scenarios for producing synthetic fuels from waste biomass.

Chapter 3: The methodology chapter evaluates and outlines the research methods used to evaluate the alternative scenarios established in Chapter 2. The research methods discussed include life cycle assessment (LCA), economic analysis and multi-criteria decision-making (MCDM).

Chapter 4: A life cycle assessment of the synthetic fuel production scenarios was conducted to evaluate the environmental impacts and benefits of alternative technological options. The chapter, aimed to carry out a detailed comparative analysis that will aid future researchers in identifying the most sustainable and feasible options for producing cleaner transportation fuels.

Chapter 5: The production costs of synthetic fuel for the range of technological options outlined in the previous chapters are analysed. A sensitivity analysis was also undertaken to identify which factors had the most significant impact on cost for each scenario.

Chapter 6: Alternative methods for holistically comparing a range of technology options for producing synthetic fuels were reviewed. The Analytic Hierarchy Process and the Technique for Order of Preference by Similarity to Ideal Solution were used to compare environmental, financial and technical data gathered throughout the thesis and recommend the most reliable scenarios to obtain sustainable synthetic fuels.

Chapter 7: This chapter debates the research outcomes of the thesis and the extent to which the original aims and objectives were met. The chapter concludes by highlighting the contribution to knowledge and the potential for further work.

Chapter 2

2. Literature review

In this chapter, a review is carried out on different thermochemical and biochemical methods for converting biomass into a bio- or synthetic fuel as well as an investigation of the use of the pyrolysis process for producing transportation fuels. Alternative reactor designs and upgrading processes for improving fuel quality required for transportation purposes are also reviewed to establish the state of the art. An outcome from the chapter is the identification of the most promising pyrolysis and upgrading combination to be investigated further for their sustainability in the thesis.

2.1. Existing biomass to bio and synthetic fuel technologies

There are many technological pathways to produce liquid fuels that are capable of replacing conventional fossil fuels. These numerous choices regarding feedstock types and subsets of technological conversion options include biofuels (bioethanol and biodiesel) produced through fermentation and transesterification (Cherubini, 2010) and synthetic fuels obtained via advanced thermochemical treatments processes (combustion, hydrothermal liquefactions, gasification and pyrolysis) (Bain, 2004). In fermentation, enzymes and microorganisms are used to obtain recoverable products (organic acids and alcohols) from a fermentable substrate (Cherubini, 2010). Combustion is mainly used to produce electricity from biomass rather than transportation fuels (Kumar, Jones and Hanna, 2009), whereas hydrothermal processes (like liquefaction) rely on water at high pressure and temperatures to act as a reactant, solvent or catalyst on biomass feedstocks in order to obtain yields of biocrude products (Savage, Levine and Huelsman, 2010). Thermochemical processing of biomass implies chemical reformation through thermal decay using various concentrations of oxygen. Heating biomass in the presence of low oxygen concentrations at high temperatures of approximately 800 - 900ºC via gasification leads to a combustible gas mixture (syngas); further, the Fischer-Tropsch process may be used to convert this gas into liquid synthetic fuel. Alternatively, heating biomass in the total absence of oxygen via pyrolysis, different organic liquids can be obtained and further upgraded to liquid fuels

(Abbasi and Abbasi, 2010). Figure 2.1 shows the various types of bio and synthetic fuels obtained by different biomass technological conversion. The figure is explained further, in Sections 2.1.1 - 2.1.11.
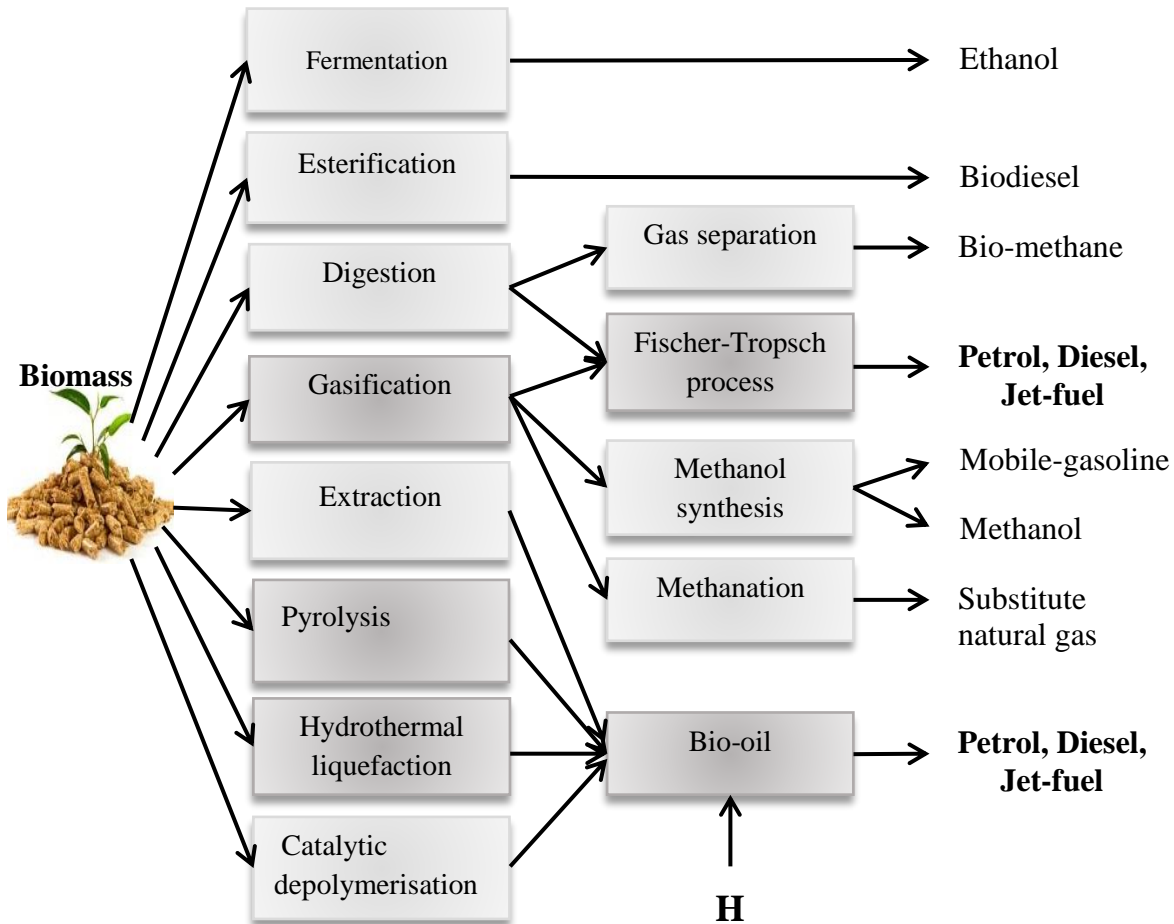
Figure 2.1: Different types of fuels obtainable from biomass - adapted after Muradov and Veziroğlu (2008)

The conversion processes of biomass into the various types of bio and synthetic fuels might require additional steps, as follows:

2.1.1. Ethanol Production

Ethanol is a clear liquid alcohol and can be produced by fermentation of various biomass feedstocks using the glucose derived from: sugars (e.g. sugar cane, sugar beet, sweet sorghum, molases), starch (e.g. corn, wheat, sorghum, tapioca, cassava) or cellulose (e.g. wood, switch grass, corn stover) (Bioenergy Australia, 2016).

The biomass-ethanol conversion method is different, depending on the feedstock type. The feedstock needs to be converted first into glucose. In the case of sugar rich plants this is straightforward, as sugar just needs to be dissolved into the water. Starch plants require some pre-processing, normally liquefaction and saccharification process to free the glucose bound in the starch by the addition of enzymes. Cellulose plants, however, require an advanced enzymatic hydrolysis process to achieve the conversion to glucose. Hydrolysis involves the degradation of hemicellulose sugars into weak acids, furan derivatives and phenols - compounds that may inhibit subsequent fermentation, resulting in reduced ethanol yields (Bioenergy Australia, 2016; Hamelinck, Van Hooijdonk and Faaij, 2005).

Comparing starch and cellulosic ethanol identifies some advantages and disadvantages. Considering the conversion process, starch refineries just need to grind the feedstock and add common enzymes – which breaks the feedstock down into glucose. For cellulosic biomass ethanol production, the process is slower and more complicated – the feedstock has to be ground before adding acid to separate hemicellulose, cellulose and lignin. Lignin constitutes around 60% of the total feedstock, and is not fermentable, so must be removed, but may also be used as a co-product to make the process more sustainable. Next, acid breaks down hemicellulose into four component sugars and cellulose is freed and broken into glucose by enzymes. While glucose is easy to convert to ethanol, other component sugars are not, so refineries need engineered microbes. Toxin build-up, incomplete conversions and slow enzymes complicate the process and reduces the ethanol yield. On the other hand, cellulosic ethanol can be produced from some waste products, therefore lowering the amount of fertilisers and water needed to grow the utilised feedstock (Hamelinck *et al.*, 2005; InfoSpace, 2018).

2.1.2. Bio-diesel Production

Biodiesel is made mainly from vegetable oils, e.g. palm, peanut, rapeseed, sunflower, coconut, palm and soya oils or animal fats whose main constituents are triglycerides (esters of fatty acids with glycerol). The main problem with the vegetable oils is the high viscosity, which can be overcome through transesterification of the fatty acids. Transesterification is a chemical reaction, which uses alcohol (usually methanol) to produce biodiesel. The process is very well established and depending on the feedstock

used, biodiesel is typically considered a first-generation biofuels (Sido-Pabyam *et al.*, 2015; Knothe, Krahl and Van Gerpen, 2015).

2.1.3. Biomethane and production

Biogas is produced from digestion of organic feedstock. Further, biomethane can be produced by the enrichment of methane content of biogas, landfill gas or sewage gas. The process is well established, around 460 biomethane plants are operating in Europe (UNIDO, 2017).

2.1.4. Substitute natural gas production

Methanation is a process required to increase the methane content of the gas obtained from gasification (converts CO_x to CH_4 through hydrogenation). Next, the obtained mixture need to be recycled into a substitute to natural gas. The disadvantage of the process consist in the large volume of gas to be processed, but also in the increase in costs and losses of energy due to the compression of the recycled gas (Tunå, 2008).

2.1.5. Methanol and mobile gasoline production

Methanol synthesis is a process subsequent gasification that helps to convert biomass into gasoline. In the methanol to gasoline process (MTG), methanol is reacted over ZSM-5 zeolite catalyst – allowing the production of gasoline and lighter material. The main advantage of the technology is that it produces a 'drop-in' fuel (completely interchangeable with conventional petroleum-derived hydrocarbons) that may be accommodated in current motor-fueled vehicles, and the process is well developed and already commercialised. The risk consists in the intensive conversion process, and the need to be blended with conventional fossil fuels to meet the current fuel specifications (Phillips *et al.*, 2011).

2.1.6. Petrol, diesel and jet fuel production

Transportation fuels that do not require further blending with fossil fuels to meet the desired specifications were found to be achievable through two main methods: by Fischer-Tropsch (FT) process, following gasification; or from bio-oil upgrading using pyrolysis process, extraction, hydrothermal liquefaction or catalytic depolimerization.

2.1.7. Fischer-Tropsch (FT) process

Gasification is a process that can convert various materials (e.g. organic materials, rubber, plastic) into carbon monoxide, carbon dioxide and hydrogen. The process takes

place at high temperatures (>700°C), and the reaction is achieved by mixing the material with oxygen and/or steam. The resulting gas is itself a fuel and is known as syngas. The advantage of syngas is that it combusts at higher temperatures than the original fuel, or even in fuel cells. Another advantage lies in the products that can be produced by burning it such as methanol and hydrogen; or through the Fisher-Tropsch synthesis to produce long chain hydrocarbons that are converted to synthetic fuel, like green diesel (Boerrigter, Den Uil and Calis, 2003; European Commission, 2016). Gasification can be performed on waste materials, such as biodegradable waste, producing clean syngas. It is a well-established process, and it is used on industrial scales to produce electricity from fossil fuels. Biomass can be converted into renewable energy by gasification, but requires feedstock stabilisation through pre-treatments such as torrefaction (European Commission, 2016).

FT reaction was discovered in 1923, when the synthesis gas was reacted with cobalt catalyst, resulting in gasoline, diesel and other distillates (Fischer and Tropsch, 1923). Although there are numerous FT plants that obtain syngas from coal gasification (fossil fuel) (Ail and Dasappa, 2016), there are just a few small scale biomass to liquid (BTL) FT plants until now. The German company CHOREN Industries established the first BTL plant in 1996, with an annual capacity of 15,000 tons of biofuel (beta plant). As the SunDiesel was demonstrated to be profitable in a large production plant with capacities of at least 100,000 t/a; CHOREN is developing standard production plants with annual capacities of 200,000 t/a. New plants are planned to be developed in Lubmina, Dormagen and Uelzen (Dautzenberg and Hanf, 2008). The Indian Institute of Science carried out state-of-the-art biomass technology development, using numerous biomass fuels (Gnanendra, Ramesha and Dasappa, 2012; Dasappa, Sridhar *et al.*, 2011; Dasappa, Subbukrishna *et al.*, 2011; Dasappa, 2011). Recent work focusing on the conversion of biomass to transportation fuels highlights that fuel conversion efficiency is dependent on biomass moisture content and also the catalysts used, which have a significant impact on fuel production rates and therefore on the liquid fuel cost (Sandeep and Dasappa, 2014; Ail and Dasappa, 2016). It was found that biomass to liquid fuel efficiency could range between 28 - 40%, but can be improved to up to 50 - 55% by using a high yielding catalyst, an efficient FT reactor design with high heat transfer rates, along with the technologies of O_2 generation, syngas purification and CO_2 separation. If the conditions are not optimised, the efficiency can decrease to 20 - 34%

(Ail and Dasappa, 2016). Likewise, a BTL pilot-plant that involved a dual fluidised bed gasifier, a methanol absorption tower, and a FT synthesis process was recently investigated. The gas was cleaned in multiple stages and produced a clean BTL fuel similar to kerosene and diesel that can be used as an alternative automotive fuel. Further research is though needed to achieve the lubricity and density standards (Y. Kim *et al.*, 2016).

FTS (the Fischer-Tropsch synthesis) process is used to produce alkanes derived from syngas using different catalysts (Fe-, Co- or Ru-based); the aim in FTS consists in producing heavy waxes and hydrocracking them to diesel and gasoline fuel, using fluidised bed, fixed bed or slurry bed reactors (G. W. Huber, Iborra and Corma, 2006; Bartholomew, 1997). A demonstration pilot plant was built by Shell and ECN in The Netherlands to explore different concepts of obtaining FTS fuels derived from biomass syngas. The process consisted in feeding wood biomass to a fluidised bed gasifier, wet gas cleaning and conditioning, followed by WGS (water-gas shift) and FTS reactions and catalytically cracking the FT waxes to obtain a high quality diesel fuel with no sulphur traces, as well as synthetic natural gas and electricity as by-products. The syngas derived liquid fuels, however, had lower thermal efficiency when compared to pyrolysis bio-oil (G. W. Huber *et al.*, 2006). Yan *et al.* (2013) studied the conversion of wood syngas into synthetic fuels for aviation using a multifunctional catalyst. The process consisted in gasification of oak tree woodchips to syngas and the resulted product was then purified to remove oxygen, ammonia, sulphur, moisture and tar; catalytic conversion on the purified syngas into liquid fuels was further developed under a multifunctional catalyst (K-Fe-Co-Mo-y- Alumina) and the gas and liquid products resulted were analysed. The obtained liquid fuels presented similar properties to those of Jet A (a commercial aviation turbine fuel).

2.1.8. Extraction process

There are various techniques used for biomass extraction: supercritical fluid extractor (SFE), ultrasound extraction (UE), microwave assisted extraction (MAE), and pressurised solvent extraction (PSE). The extraction method is chosen according to the biomass material and the components to be isolated. Extraction use different solvents (ethanol, ispropanol, methanol, water) and can produce various products, e.g. high

quality essential oils and it is mainly used in perfume, cosmetic, pharmaceutical and food industries (Segneanu *et al.*, 2013).

2.1.9. Pyrolysis process

Pyrolysis involves the thermal decomposition of matter in an oxygen free environment, and has been applied for thousands of years to produce charcoal.

It can be represented through a simple equation, presented as below (Brownsort, 2009a).
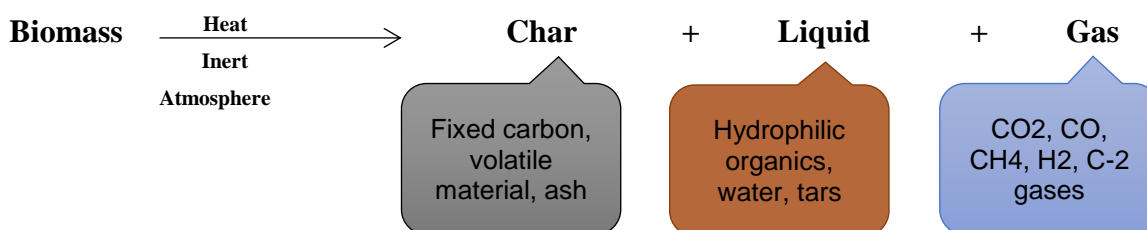
The main types of pyrolysis are Slow Pyrolysis, Intermediate Pyrolysis, Fast Pyrolysis and Flash Pyrolysis. Slow Pyrolysis is characterised by slow heating rates, long solid and vapour residence times and lower temperatures than in fast pyrolysis. The main product obtained is char, which makes it unsuitable for obtaining high-quality bio-oil (Brownsort, 2009a). Intermediate Pyrolysis is characterised by slow heating rates and intermediate solid, and vapour residence times and temperatures. It is a process that is still in research and development. Intermediate pyrolysis gives lower oil yields than fast pyrolysis, but with improved properties that are more compatible with the fuels, as recent studies has shown (Yang *et al.*, 2014). Fast and Flash Pyrolysis are characterised by high heating rates, short solid and vapour residence times and high temperatures. Fast pyrolysis was a process designed during the 1970s oil shortage, to give a higher amount of bio-oil and produce liquid fuels from indigenous renewable resources such as wood (Brownsort, 2009a), whereas flash pyrolysis is a promising process that can give up to 75% bio-oil yields. However, it presents some disadvantages such as corrosiveness of the oil, thermal instability and the presence of solids in the oil, which make it unsuitable as a transportation fuel (Cornelissen *et al.*, 2008).

The pyrolysis process is very complex and involves both simultaneous and successive reactions. In this process, organic material can be heated in the absence of air/oxygen. Thermal decomposition of feedstock components in biomass starts at 350°C - 550°C and develops up to 700°C - 800°C (Fisher *et al.*, 2002). The early pyrolysis technology

had disadvantages such as slow production, low energy yield of the product pyrolysis oil and extreme air pollution. Therefore, different methods of refining the technology were studied towards making pyrolysis a viable proposition. The aim was to recover the maximum energy or bio-oil yield from a particular type of biomass (Jahirul *et al.*, 2012). Liquid yields of up to 70 - 80% have been reported (Bulushev and Ross, 2011).

Table 2.1 illustrates the main types of pyrolysis, process conditions and the yields based on dry feedstock.

Table 2.1: Typical product weight yields (dry wood basis) obtained by different modes of pyrolysis of wood (Bridgwater, 2012a; Hossain and Davies, 2013)

Mode	Conditions	Liquid	Solid	Gas
Fast	~ 500°C, short hot vapour residence time ~ 1s	75%	12% char	13%
Intermediate	~ 500°C, hot vapour residence time ~ 10 - 30s	50% in 2 phases	25% char	25%
Carbonisation (Slow)	~ 400°C, long vapour residence time ~ days	30%	35% char	35%
Gasification	750 - 900°C	5%	10% char	85%
Torrefaction (Slow)	~ 290°C, residence time ~ 10 - 60min	0% unless condensed, then up to 5%	80% solid	20%

Most waste biomass is composed of three main natural materials: cellulose, hemicellulose and lignin. These, however, are in different proportion for each biomass type, and have different impacts on the pyrolytic process. Primary products of cellulose and hemicellulose are condensable vapours, resulting in liquid products and gas. Lignin though, decomposes to liquid, gas and char products. Extractives can affect the liquid and gas products through volatisation or decomposition; and the ash will contain most of the feedstock minerals (R. Brown, 2009; Brownsort, 2009b). Figure 2.2 below shows biomass components distribution through pyrolytic conversion.
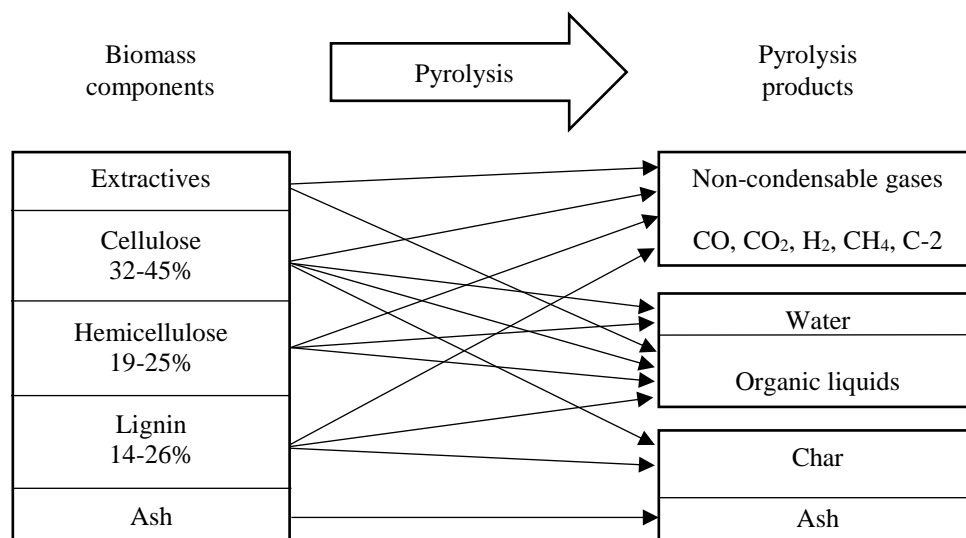
Figure 2.2: Simplified representation of Biomass Pyrolysis (R. Brown, 2009)

2.1.10. Hydrothermal liquefaction

Hydrothermal liquefaction is a process to obtain clean biofuel from biomass by using solvents at moderate to high temperatures (250 - 550 ° C). The method can process biomass with high moisture levels (unlike pyrolysis). Feedstock such as municipal and milling wastes, grasses, tropical and aquatic plantations can be conveniently extracted by the hydrothermal liquefaction process. Higher yield for raw sawdust material was reached at 350 ° C, but further temperature rise may inhibit the liquefaction process (Akhtar and Amin, 2011). A disadvantage of the hydrothermal liquefaction process is the low yield compared to other methods (such as pyrolysis), as the highest yield was found to be under 40 wt.% of the raw material (Akhtar and Amin, 2011) compared to the 70 - 80% reported for fast pyrolysis. The liquefaction of biomass into liquid fuels for transport is not currently considered to be feasible (Behrendt *et al.*, 2008).

2.1.11. Catalytic depolymerisation

Depolymerisation is the process that breaks a polymer chain to a monomer or a mixture of monomers. Depolarization process was first developed around 1980 for plastic, but the process was developed in the last decade (Zero Waste Scotland, 2013). Catalytic depolarization depends on the feedstock quality, but in case of lignin a yield of up to 43.5%, using 100% methanol as the solvent has been reported (McVeigh *et al.*, 2016).

2.2 Transportation fuels - technology selection

Having reviewed the alternative technologies from producing liquid fuels from waste biomass for transportation purposed, the decision was made to pursue fast pyrolysis further given the technologies potential and the need for further research in this field. In the last 30 years fast pyrolysis has become of considerable interest, as the process directly gives high yield of liquids of up to 60 - 75 wt% (percentage by weight), 15 - 25% biochar and other solids and 10 - 20% gaseous products (Demirbas and Arin, 2002). The liquid yield was considered a determining factor in choosing fast pyrolysis against other methods of producing transportation fuels, such as AD, Gasification, BTL or intermediate pyrolysis. Bridgwater (2012a) studied fast pyrolysis of biomass and product upgrading, and provided an updated review on fast pyrolysis of biomass for production of bio-oil. Fast pyrolysis (principles, reactors and the heat transfer), pyrolysis bio-oil, bio-oil upgrading, applications, and costs were analysed. It was found that the liquid bio-oil produced by fast pyrolysis presents important advantages, but also disadvantages considering storing and transportation. Nevertheless, its potential is increasingly being recognised and further research is taken into consideration to increase the bio-oil properties for synthetic fuel production.

2.3. Pyrolysis and pyrolysis oil research

Bridgwater (2012b) conducted a comprehensive examination analysing the quality and characteristics of bio-oil from fast pyrolysis of biomass. The objective was to upgrade the bio-oil to improve quality, by reducing or removing undesirable characteristics or properties. Some significant factors were emphasised (feed material, acidity or low pH, aging, high viscosity, toxicity, etc.) as they can affect bio-oil characteristics. The study concluded that the quality of bio-oil can be specifically affected by the aging phenomenon – which inhibits wide spread usage, acidity – which causes corrosion and nondistilability – which inhibits refining and high-oxygen content (and requires extensive removal to derive biofuels). The relatively low hydrogen content of bio-oil requires multi-stage upgrading (to overcome coking of catalysts) – i.e. the bio-oil is processed in sequential steps to give a progressively upgraded product.

Lindfors (2009) studied the composition of bio-oils obtained from forest residue, as the bio-oil produced during fast pyrolysis is highly dependent on the feedstock and the process conditions. A wide range of pyrolysis reactor configurations were investigated

and it was found that fast pyrolysis is an efficient way to produce liquid fuels from this feedstock. The quality of the bio-oil can be improved in different stages: before pyrolysis by changing the harvesting process of the forest residue; during the fast pyrolysis process the solid content in the bio-oil can be reduced by efficient char removal, and after the pyrolysis process, the quality of the bio-oil had to be improved before it could be used in the transport sector. For the latter, the addition of alcohol was used to stabilise the bio-oil, by improving some negative properties of the liquid fuel, such as the aging of pyrolysis liquid and the phase separation of extractives. During alcohol dilution the viscosity and density of the bio-oil decreased, while the phase separation of extractives increased. It was concluded that to obtain a liquid fuel comparable with fossil fuels, the oxygen and water content in the bio-oil has to be reduced.

Pyrolysis behaviour for various types of biomass was studied by Părpăriţă *et al.* (2014). The thermal behaviour of different types of biomass was evaluated by thermogravimetry and by analytical pyrolysis. The biomass used was: forestry – Eucalyptus globulus sawdust, Norway spruce; agricultural – energy grass (Szarvas), Brassica rapa; and by-products – pine cones, grape seeds. The liquid obtained through pyrolysis was analysed, and the elemental analysis and the calorific values of the pyrolysis residues were investigated. It was established that the pyrolysis products resulted from the degradation of the main structural components of biomass and consisted mainly of: ketones, carboxylic acids, furans, phenols, catechols, guaiacols and their derivatives (Parparita *et al.*, 2014). It was found that the biomass source is a determinant factor regarding the distribution of compounds in oils, as differences in the pyrolysis behaviour among the biomass samples were identified.

Unlike FT, the pyrolysis process is not so well established, but a number of pyrolysis reactors have been developed: fixed bed, fluidised bed, circulated bed, rotating cone, ablative, screw feeder/auger and vacuum pyrolysers (Bridgwater, 2012a; Iribarren *et al.*, 2012; Deng, Liu and Cai, 2008; Meier and Faix, 1999) (see Section 2.2), and several technologies have reached the commercialisation stage (Strezov and Evans, 2014). The main reactors commercialised or at stage of demonstration, pilot and laboratory research are bubbling and circulated fluidised bed and rotating cone reactors (Kan, Strezov and Evans, 2016). Some organizations developed fast pyrolysis systems for converting

biomass to bio-oil by thermal, non-catalytic processes: DynaMotive – University of Waterloo, Canada – uses a bubbling fluidised bed reactor to heat a feedstock with less than 10% moisture and 3 mm in size at approximately 430°C for longer than 3 seconds and obtained yields of 50 - 75% (Scott *et al.*, 1999; Piskorz, Majerski and Radlein, 1998a; Piskorz, Majerski and Radlein, 1998b); Ensyn – University of Western Ontario Canada – uses a large scale circulated bed transport reactor to heat a feedstock with up to 10% moisture and 6mm at 500 - 700°C for 100 - 600ms, with bio-oil yields of 66 - 90wt% (Graham, Bergougnou and Freel, 1994); BTG rotating cone reactor (RCR) – BTG was invented and developed at the University of Twente Netherlands, but a first prototype was shipped to the Shenyang Agricultural University of China in 1994, and a novel version that included an interconnected fluidised bed for char combustion was developed (Janse *et al.*, 2000) and a demonstration plant was established in Genting, Malaysia (Venderbosch and Prins, 2010) – the rotating cone reactors were used at 300 - 600 rpm to convert feedstock of sizes up to 10mm at approximately 500°C to deliver bio-oil yields of 70 - 75wt% (Venderbosch and Prins, 2010). There are several more pyrolysis systems developed worldwide (Perkins, Bhaskar and Konarova, 2018), but because their liquid yields did not exceed 50wt% they have not been further considered. Other technologies at research and development stage are: microwave-assistant pyrolysis (Wu *et al.*, 2014; Mushtaq, Mat and Ani, 2014; Motasemi and Afzal, 2013; Abubakar and Ani, 2013; Salema and Ani, 2012; Lam, Russell and Chase, 2010; Menéndez *et al.*, 2004), hydrothermal pyrolysis (Swadchaipong *et al.*, 2013; Sasaki and Goto, 2009), and catalytic pyrolysis (Kelkar *et al.*, 2014; Hong *et al.*, 2013; Fan *et al.*, 2013).

In the UK some pyrolysis systems that produce liquid fuels have been developed, some are commercial but most of them are at Laboratory or R&D scale. Cynar (CynFuels) was founded in 2004 and recycles end-of-life plastic waste (non-recyclable plastics) into low sulphur diesel, kerosene and light oil. It has a pilot plant in Ireland, commercial plants in the UK and EU and plans to expand in Latin America and Florida. The fuel consists of approximately 70% diesel, 20% light oil and 10% kerosene. The gas obtained through pyrolysis is recycled to heat the system and 5% char that results can be commercialised as a co-product (EBRI, 2015). Future blends, Oxfordshire has a bench scale unit and a pilot plant, each using novel filtration techniques to produce a more stable and cleaner pyrolysis oil (EBRI, 2015). Aston University developed an

intermediate pyrolysis system (auger reactor) and achieved up to 51 - 54% liquid fuel from rice husks and corn stalks (Yu *et al.*, 2016). Other UK based systems for producing liquid oils systems can be found at University College London (fast catalytic pyrolysis) – bench scale, University of Cambridge (microwave pyrolysis) – commercial scale. University of Leeds – bench scale (EBRI, 2015).

Biomass pyrolysis is a promising technology for bioenergy development, but in order to enhance its potential some limitations need to be overcome: feedstock pretreatment, reliability of the reactors and reactor scalability, poor product quality, and high oxygen content compared with regular hydrocarbon fuels; and the need for new product standards to be applied (A. Sharma, Pareek and Zhang, 2015; Lede, 2013; Jahirul *et al.*, 2012). Additional to pyrolysis downstreams, technology development is required to obtain final products with high added value (Kan *et al.*, 2016). Therefore, different aspects have to be researched to improve the bio-oil quality to transportation fuels. If numerous research and development was done regarding pyrolysis process, the upgrading processes to transportation fuels are still into an early stage, and just a few studies have been carried out (Y. Zhang, 2014; S. Jones *et al.*, 2013; Han *et al.*, 2013; S. B. Jones and Male, 2012; Wright *et al.*, 2010b; S. B. Jones *et al.*, 2009; R. C. Brown and Holmgren, 2009; Marker *et al.*, 2005). However, all of them limited their studies to bio-oil upgrading by hydrotreating or by hydrotreating in conjunction with hydrocracking processes. These upgrading processes produced fuels compatible with gasoline and diesel, but with higher oxygen content and high acidity and viscosity. Therefore, further research is needed to improve the quality of liquid fuel by reducing the oxygen content, acidity and viscosity and to achieve fuels with longer hydrocarbon chains, compatible with kerosene, for application in the aviation industry.

To achieve the aim of the project - to produce sustainable transport fuels from waste biomass, and considering the limited existing processes and technology and the lack of research, it was decided to research and analyse different methods of upgrading the pyrolysis oil to sustainable transport fuels.

2.3.1. Pyrolysis reactors

Reactor can be perceived as the heart of any pyrolysis process. A number of models of pyrolysis reactors have been designed and analysed in order to improve the essential pyrolysis characteristics: heating rates, temperature and vapour residence times for

liquid. Initially, pyrolysis reactors were designed to use a short vapour residence time and small particle size (less than 1mm) to achieve a high bio-oil yield. Later research showed that the vapour residence time and the particle size have less impact on bio-oil yield, but significantly influence the bio-oil composition (Jahirul *et al.*, 2012). Therefore, various pyrolysis designs have been developed and optimised to produce higher quality bio-oil. Each pyrolysis reactor design has specific characteristics, advantages and limitations. The most used reactors include the fixed-bed, fluidised bed reactor, Bubbling fluidised bed, circulating fluidised bed, ablative , vortex, rotating disk, vacuum pyrolysis, rotating cone, PyRos, auger, plasma, microwave and solar reactor (Jahirul *et al.*, 2012).

The main reactor types are now described:

2.3.1.1. Fixed bed fast pyrolysis

 A fixed bed pyrolysis reactor, heated by means of a cylindrical biomass source heater was designed and fabricated by Hossain et al. (2014). The main components of the system were: the fixed bed reactor, liquid condenser and liquid collectors. It was found that the variable parameters (reactor bed temperature, running time and feed particle) had a high impact on the product yields. The maximum liquid yield of 52%w.t. was obtained at 500ºC when the feed size was smaller than 1.8mm. The authors proposed some further research regarding the temperature control through a well-insulated system. They further identified the need for the char products and the nitrogen consumption to be improved, as they were relatively high. A similar model constructed by Uddin et al. (2012) found that these variable parameters had a significant influence on the product yield. A maximum liquid yield of 39% was found at 520ºC for a feed size of 2.36 - 4.75mm. The basic design of a pyrolysis Fixed Bed Reactor is represented in Figure 2.3. Scaling up a fixed bed reactor for commercial operations is not considered to be feasible (Bridgwater, 2012a).
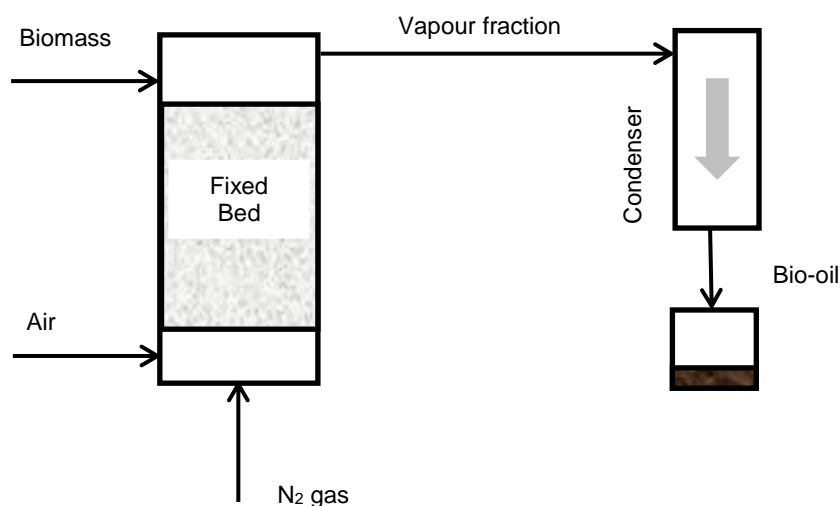
Figure 2.3: The Fixed Bed Reactor - adapted from (Hossain *et al.*, 2014; Uddin *et al.*, 2012)

The fixed bed fast pyrolysis was simulated in Aspen Plus environment using a Gibbs reactor by Liu *et al.* (2014) to analyse the balance of bio-oil pyrolysis products at different process temperatures. The modelling and the experimental results were compared and found to be similar. The methodology consisted of calculating the molar heat capacity in constant pressure conditions for the chemical balance system through simulation, determining the reactor's thermodynamic parameters through thermodynamic equations combined with the mass balance principle, calculating the conversion rate and temperature distribution of various catalyst beds through the Runge-Kutta method combined with Matlab software. The temperature was found to be an important factor for the pyrolysis of the bio-oil aqueous fraction. High temperatures helped increase the yield of H_2 and CO and reduce the carbon yield. It was also found that the catalytic pyrolysis of bio-oil was considerably influenced by the length of the reactor.

2.3.1.2. Bubbling Fluidised Bed Reactors

Bubbling fluidised bed reactors are relatively simple to construct and operate. Some of the advantages offered by this type of reactor are: better temperature control, very efficient heat transfer to biomass particles and storage capacity due to the solid density in the bed (Jahirul *et al.*, 2012; Bridgwater, 2012a).

Heated sand, used in the first phase of the fluidised bed rapidly heats the biomass in an oxygen free environment, to decompose it into: char, vapour, gas and aerosols. Next, the charcoal is removed by a cyclone. The vapour is then passed through a quenching system that condenses it to produce bio-oil (Jahirul *et al.*, 2012).

The bubbling fluidised bed is a popular reactor because of its advantages: it produces high quality bio-oil of liquid yields about 70% - 75%, char does not accumulate in the fluidised bed, and the residence time in both solid and vapour phase can be controlled by the fluidising flow rate. A disadvantage of this type of reactors is that very small particle sizes of less than 2 or 3 mm are required to achieve high biomass heating rates (Jahirul *et al.*, 2012). Figure 2.4 presents the Bubbling fluidised bed reactor.
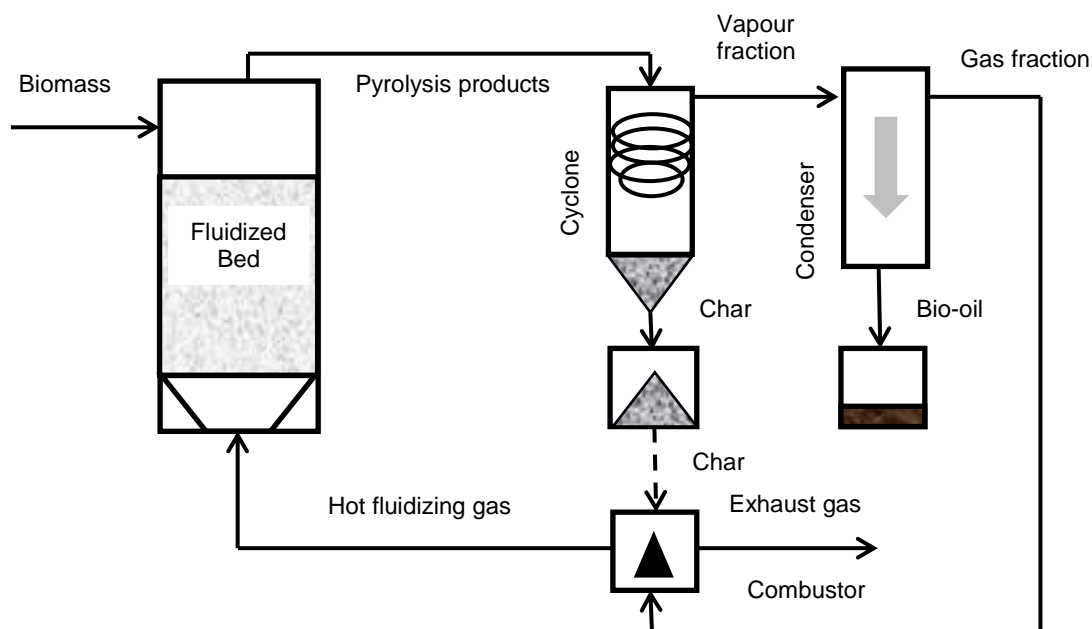
Figure 2.4: The Bubbling Fluidised Bed Reactor - adapted from (Iribarren et al., 2012; Hossain and Davies, 2013; Bridgwater, 2012a; Venderbosch and Prins, 2010)

A laboratory scale fluidised bed pyrolysis system was designed, fabricated and analysed by Islam, Islam and Nabi (2004) to obtain bio-oil. They achieved a maximum liquid yield of 50wt% at an optimum reactor temperature of 425ºC, 30l/min gas flow rate and feedstock size of 0.3mm - 0.6mm. The obtained bio-oil properties were compared with other biomass pyrolysis oils and petroleum products. The physical properties analysis indicated that the pyrolysis oil had a heavy and acidic nature, moderate viscosity and favourable pour and flash point. The lower heating value (net calorific value) was comparable with other biomass derived bio-oils. As the liquid analyses revealed a high oxygen content, it is important to deoxygenate the bio-oil to improve its quality.

2.3.1.3. Circulated Fluidised Bed

The circulated fluidised bed reactor is similar with the bubbling fluidised bed reactor except shorter residence times are used. The disadvantage is that the bio-oil has higher char contents, so the process requires extra char removal. The advantage is that the reactor is suitable for very large quantities of feedstock (Jahirul *et al.*, 2012; Bridgwater, 2012a). The fluidised bed reactor is considered to have a high commercial potential for the pyrolysis of biomass. Lab-scale batch experiments and pilot-scale circulated fluidised bed experiments have achieved oil yields between 60 and 70wt% (Venderbosch and Prins, 2010; Van de Velden, Baeyens and Boukis, 2008) at an optimum temperature of 510°C (Van de Velden *et al.*, 2008). Figure 2.5 presents the Circulated Fluidised Bed Reactor.
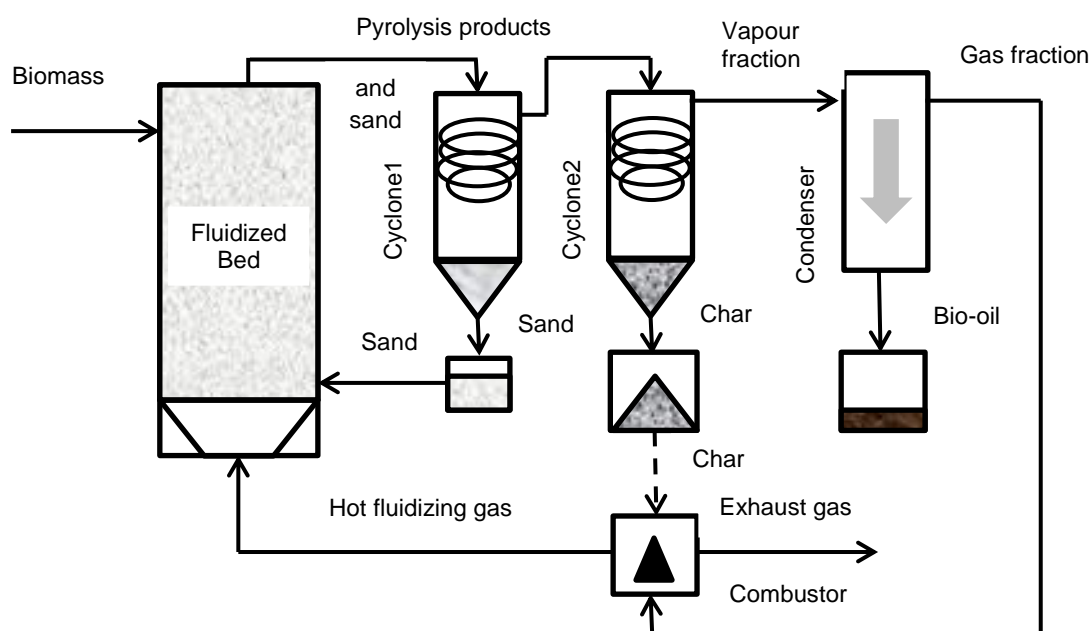
Figure 2.5: The Circulated Fluidised Bed Reactor - adapted from (Iribarren et al., 2012; Hossain and Davies, 2013; Bridgwater, 2012a; Venderbosch and Prins, 2010)

2.3.1.4. Rotating Cone

The rotating cone reactor is a relatively recent development and an effective way to transfer heat to biomass in the pyrolysis process, because of the intense mixing of biomass and hot inert particles. The biomass and sand are introduced at the base of rotating cone. The pyrolysis of the biomass feedstock is achieved by centrifugal forces in the rotating cone. Through spinning, the solid is moved upwards to the lip of a cone.

The advantage of these reactors is a high bio-oil yield 50 - 70wt%, but also feedstock with a high moisture content (70%) can be used and dried to 5% moisture using excess heat from the pyrolysis process (Venderbosch and Prins, 2010). The disadvantages of these types of reactors are that the design of rotating cone is complex, and the fluidised bed mixing requires a large amount of ineffective inert gas. Figure 2.6 shows the Rotating Cone Reactor.
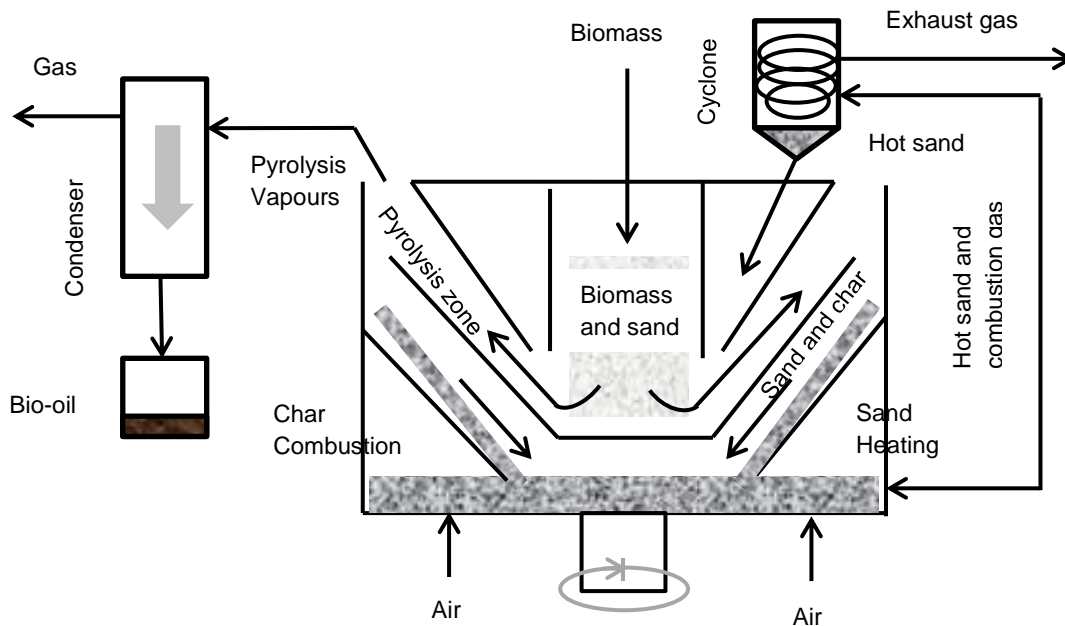
Figure 2.6: The Rotating Cone Reactor - adapted from (Iribarren et al., 2012; Hossain and Davies, 2013; Bridgwater, 2012a; Venderbosch and Prins, 2010)

2.3.1.5. Ablative Reactor

Ablative reactors are fundamentally different in concept compared with the other fast pyrolysis reactors. In this method, the heat is transferred through mechanical pressure, by pressing the biomass against a heated reactor wall. The advantage of these reactors is that the process allows larger biomass particles (up to 20mm) to be used. The disadvantage is that due to the mechanical nature of the process it requires a more complex configuration (Jahirul *et al.*, 2012; Bridgwater, 2012a). The main ablative reactors are: rotating disk and vortex.

2.3.1.5.1. Rotating Disk Reactor

The rotating disk reactor forces the feedstock to slide onto a hot rotating disk. The pyrolysis reaction is caused by biomass softening and vaporisation, in contact with the hot rotating disk at approximately 600ºC (Venderbosch and Prins, 2010). One

advantage of this reactor is that no inert gas is required. The disadvantage is that the process is dependent on surface area, as all feedstock has to come into contact to the rotating disk, so an existing system cannot be scaled for larger facilities. Figure 2.7 shows the Rotating Disk Reactor.
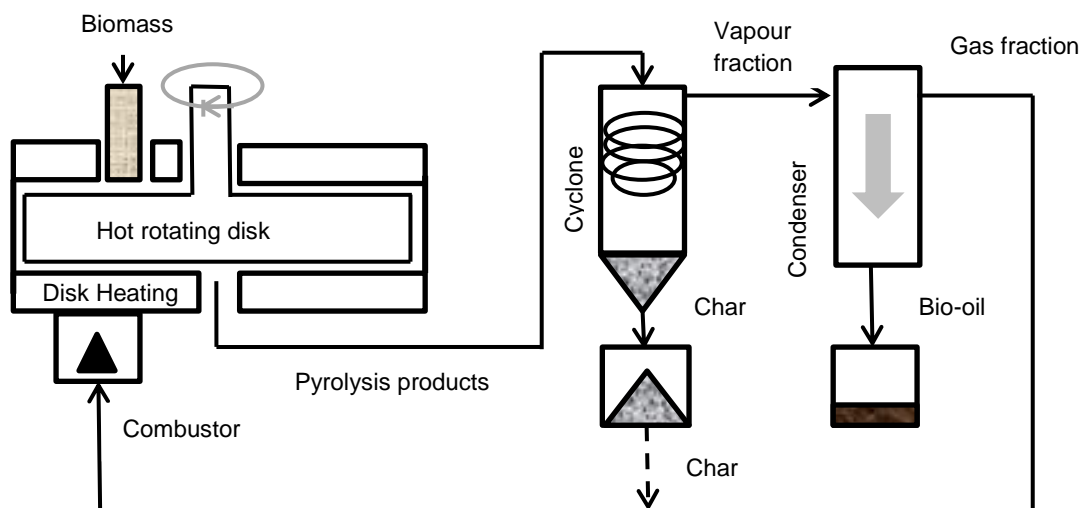
Figure 2.7: The Rotating Disk Reactor - adapted from (Iribarren et al., 2012; Venderbosch and Prins, 2010)

2.3.1.5.2. Vortex Reactor

In a vortex reactor, the biomass particles are entrained in a hot inert gas flow, entering into the reactor tube tangentially. By using the centrifugal force, the biomass particles are forced to slide on the reactor wall. The biomass particles are then melted on the hot wall, resulting into bio-oil. The advantage of this design is that has demonstrated a bio-oil yield of 65%. Figure 2.8 shows the Vortex Reactor.
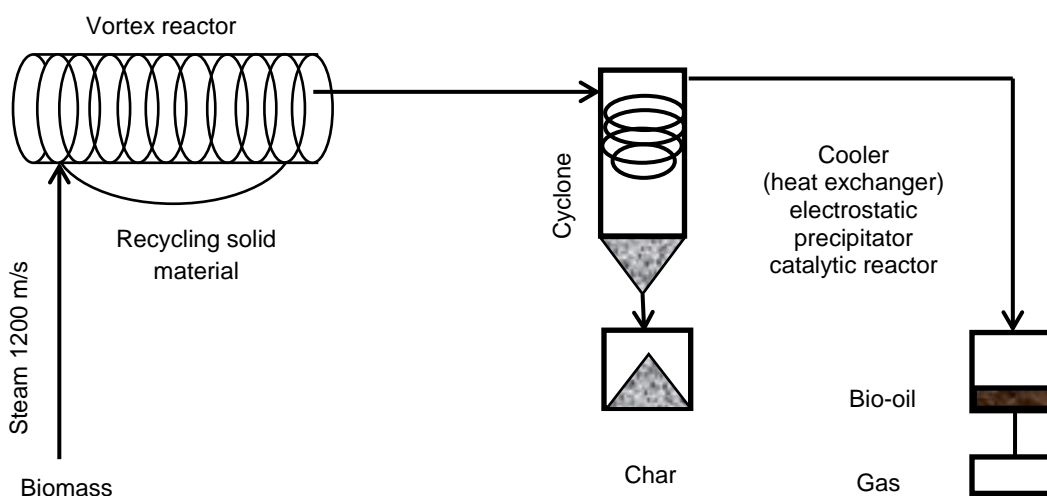
Figure 2.8: The Vortex Reactor - adapted from (Meier and Faix, 1999)

2.3.1.6. Auger Reactor – Twin Screw

Auger reactors are used to carry the biomass feedstock through an oxygen free cylindrical heated tube. Temperatures ranging from 400ºC to 800ºC cause the feedstock to gasify, with non-condensable gases then being separated from the bio-oil. The advantage of this design is that vapour residence time can be accurately altered by changing the heated zone crossed by the condenser. Figure 2.9 illustrates the Auger Reactor.
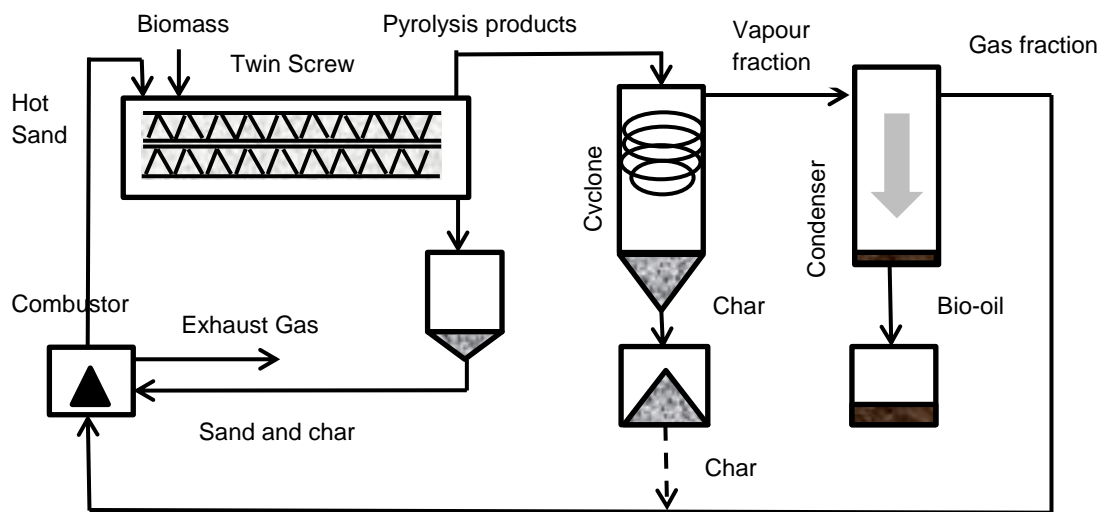
Figure 2.9: The Auger Reactor - adapted from (Iribarren et al., 2012; Hossain and Davies, 2013; Bridgwater, 2012a; Venderbosch and Prins, 2010)

2.3.1.7. Vacuum Reactor

The vacuum reactors implement a slow pyrolysis process. The feedstock is carried into a high temperature chamber, by a metal belt. A mechanical agitator periodically stirs the biomass. A burner and an introduction heater are used to heat the biomass. The disadvantage is that the liquid yield is 35 - 50% compared with 75% from a fluidised bed reactor. The vacuum reactor is complicated mechanically, requiring high investment and maintenance costs. The main advantage of this type of reactor is that can process larger sizes of biomass particles (2 - 5mm). Figure 2.10 illustrates the Vacuum Reactor.
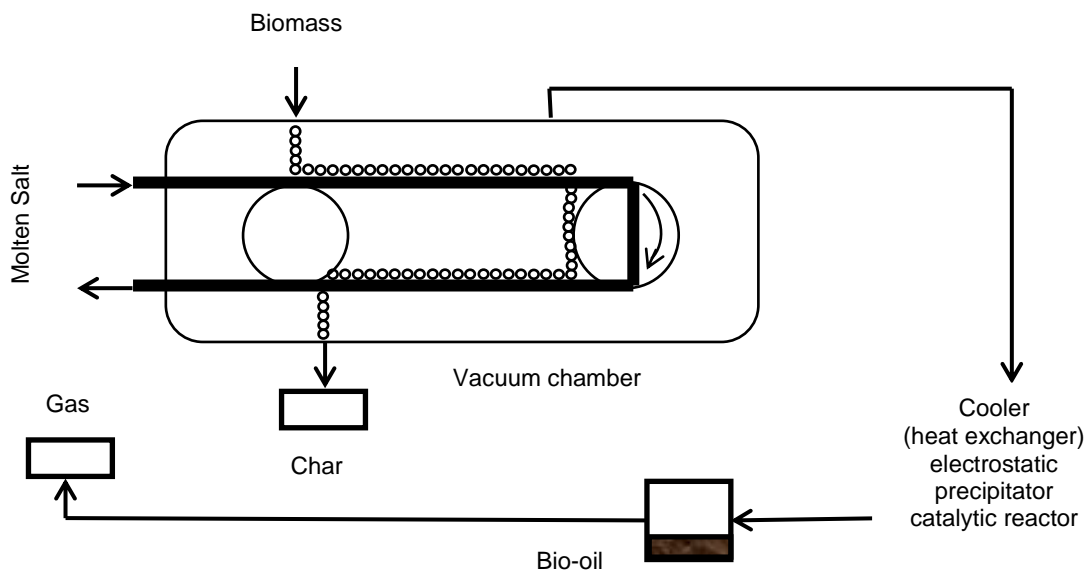
Figure 2.10: The Vacuum Reactor - Adapted from (Meier and Faix, 1999; Hossain and Davies, 2013; Venderbosch and Prins, 2010)

All the reactors presented above have different advantages and limitations. Table 2.2 summarises the advantages, disadvantages and bio-oil yield of different pyrolysis reactors.

Table 2.2: Advantages, disadvantages and bio-oil yield of different pyrolysis reactors (Ringer, Putsche and Scahill, 2006; Lam et al., 2010; Menéndez et al., 2004; Zhao et al., 2001; Scott et al., 1999)

Reactor type	Advantages	Disadvantages	Bio-Oil Yield
Fixed bed	Simple design Reliable Biomass size independent	High carbon conservation Long solid residence time Low ash carry over Difficult to remove char	35%–50%
Bubbling fluidised bed	Simple design Easy operation Good temperature control Suitable for large scale	Small particle sizes are needed	70%–75%
Circulating fluidised bed	Well-understood technology Good thermal control Large particle sizes can be used	Unlikely to be suitable for large scale Complex hydrodynamics Char is finer	70%–75%

Reactor type	Advantages	Disadvantages	Bio-Oil Yield
Rotating cone	Centrifugal force moves heated sand and biomass No carrier gas required Less wear	Complex process Small particle sizes needed Not proven yet for large scale	65%
Vacuum	Produces clean oil Can process larger particles of 3–5 cm No carrier gas required Lower temperature required Easier liquid product condensation	Slow process Solid residence time is too high Require large scale equipment Poor heat and mass transfer Generates more water	35%–50%
Ablative	Inert gas is not required Large particle sizes can be processed System is more intensive Moderate temperature required	Reactor is costly Low reaction rate Low reaction rate	70%
Auger	Compact No carrier gas required Lower process temperature	Moving parts in hot zone Heat transfer at large scale is not viable	30%–50%
PyRos	Compact and low cost High heat transfer Short gas residence time	Complex design Solids in the oil Alkali dissolved in the oil High temperature required	70%–75%
Plasma	High energy density High heat transfer High temperature Very good control	High electrical power consumption High operating costs Small particle sizes required	30%–40%
Microwave	Efficient heat transfer Exponential control Compact High heating rate Large size biomass can be processed Uniform temperature distribution High temperature	High electrical power consumption High operating costs	60%–70%
Solar	Use renewable energy High heating rate High temperature	High costs Weather dependent	40%–60%

Depending on the desired products, a variety of different pyrolysis processes, reactors (with appropriate heating methods and temperatures) and biomass feedstock can be

used. Table 2.3 shows the recommended pyrolysis technology to produce bio-char, bio-oil and syngas, the temperature required and the possible feedstock.

Table 2.3: Recommended pyrolysis technology according to product (Jahirul et al., 2012)

Product		Pyrolysis Type	Reactor	Heating Method	Temp(°C)	Biomass
Bio-char		Slow	Fixed bed	Furnace or kilns	<300	Walnut shell, olive husk, hazelnut shell
Bio-oil	Large scale	Fast	Bubbling fluidised bed	Heated recycle gas	450–550	Agriculture residue, wood chip, fruit shell
	Medium scale	Fast	Circulating fluidised bed	Wall and sand heating	450–550	Forest residue, municipal waste, dry wood, waste tyres
	Small scale	Flash	PyRos	PyRos heating	450–550	Grass, husk, wood dust
Syngas		Slow/Fast	Microwave	Electromagnetic	>800	Rice husk, wood dust

2.3.2. Pyrolysis Bio-oil

Pyrolysis bio-oil contains oxygenated compounds (acids, alcohols, aldehydes), and typically has an oxygen content of 20 - 40wt% and 15 - 30wt% water; because of the high oxygen and water content its heating value (approximately 17 MJ/kg) is inferior to that of fossil fuels (45 MJ/kg) (Oasmaa and Czernik, 1999). However, Balat *et al.* (2009) and Chiaramonti *et al.* (2007) have studied the bio-oil resulted from condensing vapours from the pyrolysis reaction and found that it presents heating values of 40 - 50% compared to fossil fuels. Several advantages were also highlighted, such as a positive balance of carbon dioxide, the possibility of using it in existing power plants at both small and large-scale and relatively effective ways of transportation and storage. There are, however, limitations in the fuel quality.

Oasmaa and Meier (2005) have found that due to the large number of constituents (300 to 400) – (Evans and Milne, 1987) there are issues regarding bio-oil stability, phase separation, viscosity when stored for longer periods of time, corrosiveness and economic viability of the thermal processing. Due to these limitations pure bio-oil can only be used in low speed diesel engines. In order to be used in high speed engines the bio-oil has to be upgraded (Chiaramonti *et al.*, 2003). Table 2.4 shows some typical bio-oil properties in comparison to biodiesel and conventional fuels.

Table 2.4: Typical properties of bio-oil (bio-crude) compared to biodiesel and conventional fuels

Property	Pyrolysis bio-oil	Biodiesel	Fuel Oil	Gasoline	Diesel
Carbon [wt%]	54 to 58	77	85	85	86 to 87
Hydrogen [wt%]	5.5 to 7.0	12	11.1	15	13
Oxygen [wt%]	35 to 40	11	1	0	0
Water [wt%]	15 to 30	<0.05	0.025	0	0.02
Solids [wt%]	0.01 to 1	-	0	-	0
Nitrogen [wt%]	0 to 0.4	-	0	-	0.065
Sulfur [mg/kg]	Negligible	Negligible	0 to 10	0.1	0 to 10
Ash [wt%]	0.01 to 0.2	0.2	0.01	-	0.01
Acidity [pH]	2 to 3	0 to 14	Neutral	-	5.5 to 8
Visosity (40ºC) [cP]	13 to 35	4 to 6	3.0 to 7.5	0.44	1.3 to 4.1
Density (15ºC) [kg^{-3}/m^3]	1.10 -1.30	0.88	0.89	0.68	0.82-0.84
Stability	Unstable	-	Stable	-	Stable
LHV [MJ/kg]	13 to 18	39	40.3	42	42 to 43
Flash point [ºC]	40 to 110	100 to170	60	23	60 to 80
Pour point [ºC]	-9 to -36	-15 to 10	-15	-20	-15 to -35
Boiling range [ºC]	Decomposes	315-350	160-400	78	180-369.8
Cetane number	40-56	48-65	38-40	17	40-55
Refs:	(Oasmaa and Czernik, 1999), (Ikura, Stanciulescu and Hogan, 2003), (Huber and Corma, 2007), (Zhang *et al.*, 2007), (Bridgwater, 2012), (Oasmaa, Kuoppala and Elliott, 2012), (Chong and Bridgwater, 2017)	Education Laboratory, 2011), (Herskowitz *et al.*, 2012), (Biorenewables	(Oasmaa *et al.*, 2012)	(Chaichan, 2014), (Panda, Singh and Mishra, 2010)	(Biorenewables Education Laboratory, 2011), (Herskowitz *et al.*, 2012), (Chaichan, 2014), (Government Fleet, 2016)

* Note: Measurement of flash point of bio-oil is problematic due to water evaporation and difficulty in sustaining flame.

2.4. Bio-oil upgrading technologies

Bio-oil needs to be upgraded so that it can be used in the transportation and aviation industry. Bridgwater (2012a) conducted a review on product upgrading and found that there are several pathways of upgrading bio-oil to bio-fuel: physically, through filtration, solvent addition and emulsions; chemically, via aqueous phase processing, mild cracking, esterification and other processes, hydrogenation by steam reforming or gasification for synfuels, and catalytically, by cracking high molecular weight components in light hydrocarbon products in order to improve pyrolysis reaction kinetics (Ahmed and Gupta, 2010).

2.4.1. Physical upgrading

Diebold *et al.* (1994) have studied hot-vapour filtration of bio-oil; they found that a high quality product can be obtained, containing lower char quantities, and reduced ash and alkali content, but the resulting yield may lack economic efficiency, as it is produced in low quantities. Diebold and Czernik (1997) added solvents to reduce the viscosity of bio-oil; their study showed that the addition of methanol significantly improves the quality of bio-oil. Research has been also carried out on emulsifying pyrolysis oil with diesel oil using surfactants to produce transportation fuels; however, very high levels of corrosion were noticed when compared to diesel and bio-oil, and the production costs were also high (Baglioni, 2001).

2.4.2. Catalytic upgrading

Catalysts improve the chemical reaction kinetics in the pyrolysis process by cracking molecular weight components in light hydrocarbon products (Ahmed and Gupta, 2010). Depending on composition, catalysts were divided into Ni-based, dolomite (calcined dolomite being used extensively as it is cheaper and reduces tar formation up to 90 - 95%), and alkali metal and novel metal catalysts (Hu *et al.*, 2006), which can achieve more than 99% tar removal (Han and Kim, 2008). Catalysts may be added to the feedstock before it is fed to the reactor (Demiral and Şensöz, 2008), inside the reactor (He *et al.*, 2009) or in a secondary reactor (Hao *et al.*, 2003). There are, however, limitations in using catalysts; for instance, calcined dolomite has a low melting point (He *et al.*, 2010) whereas alkali and Ni based catalysts may be deactivated by carbon deposition and have only been researched in small-scale lab conditions (Han and Kim, 2008). The most used catalysts in petrochemistry and oil refining are zeolites (Corma,

2003), hence their use for upgrading bio-oil was studied to enhance thermal stability and to reduce the oxygen content. Zeolite upgrading on wood-derived fast pyrolysis oils under different catalysts was studied by Sharma and Bakhshi (1993), Katikaneni *et al.* (1995) and Adjaye *et al.* (1996); they found that the process takes place at temperatures of 350 - 500°C and results in hydrocarbons (aliphatic and aromatic), water, water and oil-soluble organics, gases (CO, CO_2, alkanes) and coke. The reactions that occur are dehydration, cracking, deoxygenating, polymerisation and aromatization. The hydrocarbon yields are of lower quality and high yields of coke were observed (which limits the use of the obtained product) compared to hydrotreating (Bridgwater, 1994).

2.4.3. Torrefaction

Torrefaction is a thermal pre-treatment technology used to upgrade ligno-cellulosic biomass to higher quality biofuel by removing the oxygen under a low temperature range of approximately 200 - 300°C (Pach, Zanzi and Björnbom, 2002). Van der Stelt *et al.* (2011) reviewed torrefaction to analyse whether it improves biomass properties and offers solutions to biomass limitations; they found that the main advantage of torrefaction is improvement of energy density and grindability. Further research can be done on the kinetics of the reactor design and on product characteristics such as pelletization, biological degradation or dust forming of the solid biomass. Atienza-Martínez *et al.* (2015) used torrefied sewage sludge in a fast pyrolysis fluidised bed reactor to find out if torrefaction pre-treatment improves the properties of the pyrolysis bio-oil. The experimental results revealed that the homogeneity of the liquid was not improved, even though it reduces water and liquid aqueous content.

2.4.4. Hydrodeoxygenation

Hydrodeoxygenation refers to the hydrotreatment process that uses hydrogen and catalysts to reduce the oxygen content in bio-oil (Ahmad, Nordin and Azizan, 2010). It occurs when bio-oil is treated with high pressure H_2 under moderate temperatures of approximately 300 - 600°C, using heterogenous catalysts (usually NiMo and CoMo-based) in a two-step process. Compared to untreated bio-oil, the upgraded product presents significantly lower ratios of oxygen and sulphur; moreover, it has a lower octane number than gasoline, which makes it more eco-friendly (D. Elliott and Schiefelbein, 1989). Elkasabi *et al.* (2014) have analysed how fast-pyrolysis bio-oils – derived from various feedstocks such as *Eucalyptus benthamii*, Switchgrass, or equine

manure – behave under the hydrodeoxygenation with carbon-supported catalysts. They used Ru, Pt and Pd catalysts on carbon supports at 320°C, for 4 hours in a 2100 psi H_2 atmosphere on the three types of feedstock and the resultant products were compared; it was found that Switchgrass bio-oil under Pt/C presented the best yields in terms of hydrogen consumption, deoxygenation efficiency and the variety of upgraded bio-oil constituents. Kim et al.(2014) used hydrodeoxygenation to upgrade crude bio-oil derived via fast pyrolysis from woody biomass. The resulting products consisted two oil phases (light and heavy oil), as well as gas and char, their distribution was found to be highly influenced by catalyst loading, time and reaction temperature. The presence of Pd/C in suitable amounts prevented unfavourable reactions such as char and gas-phase component formation. Table 2.5 illustrates the bio-oil properties before and after HDO process.

Table 2.5: Properties of Pyrolysis Oil and Hydrotreated Bio-Oil (a comparison between upgraded bio-oil and crude bio-oil based on the reviewed literature was also made) (Huber et al., 2006)

Property	Flash pyrolysis	HDO bio-oil
Carbon (wt%)	43.5	85.3-89.2
Hydrogen (wt%)	7.3	10.5-14.1
Oxygen (wt%)	49.2	0.0-0.7
Sulfur (wt%)	29.0	0.005
H/C-ratio (dry)	1.23	1.40-1.97
Density (g/mL)	24.8	0.796-0.926
Moisture (wt%)	24.8	0.001-0.008
Higher heating value (MJ/kg)	22.6	42.3-45.3
Viscosity (cP)	59 (40oC)	1.0-4-6 (23oC)

2.4.5. Hydroprocessing

The process of hydrotreating and hydrocracking is often referred to as hydroprocessing. Hydrotreating involves the use of hydrogen and catalysts to reduce levels of sulphur, nitrogen and oxygen. For example, oxygen can be rejected as water through a catalytic reaction with hydrogen. The process takes place at relatively modest temperatures (150°C - 400°C) (T. R. Brown *et al.*, 2012; Butler *et al.*, 2011; Gandarias and Arias,

2013) and is also known as hydrodeoxygenation. To obtain higher degrees of deoxygenation and minimise the hydrogenation of aromatics, two-stage hydrotreating can be used. In the first stage, reactive and unstable compounds are transformed into more stable ones at a relatively low temperature (270ºC, 136 atm H_2) and without the use of catalysts. In the second stage, higher temperatures (400ºC, 136 atm H_2) and hydrotreating catalysts are used (D. C. Elliott, 2007). Once bio-oil has undergone hydrotreating, it can be hydrocracked to break carbon-carbon bonds and converted into shorter-chain hydrocarbons, which are more suitable as transportation fuels (T. R. Brown *et al.*, 2012). Fluid catalytic cracking (FCC) is an alternative upgrading pathway for bio-oil. Even though FCC has been considered for transport fuels in some studies (Kaufmann *et al.*, 2000), the main products from this process are chemical commodities, rather than potential transportation fuels (T. R. Brown *et al.*, 2012). Vapour catalytic cracking can improve stability, heating value and phenol content; however, acid reduction is limited, which is a problem for use as liquid transportation fuel (Lu *et al.*, 2010).

Huber and Corma (2007) studied the chemistry, catalysts and the main challenges in the production of biofuels. They have found that the processing of the biomass-derived feedstocks (cellulosic, starch-derived biomass, sugar-derived biomass, vegetable fats, etc.) by catalytic cracking and hydrotreating is a promising alternative to produce biofuels, and the existing infrastructure of petroleum refineries is well-suited for the production of biofuels, allowing a rapid transition to a more suitable economy without large capital investment for new reaction equipment; however, the triglyceride molecules need catalysts with larger pore size to prevent diffusion.

Hydrotreating and hydrocracking catalysts to process refinery oil mixtures and waste soya oil was studied by Tiwari *et al.* (2011); they used low acidic alumina and moderately acidic mesoporous silica-alumina support catalysts to produce pure hydrocarbon mixtures that can be used as kerosene and diesel by hydroprocessing mixtures of waste soya-oil and gas oil. Their findings show that hydrotreating and hydrocracking bio-oils with petroleum fractions is a viable process and that for obtaining kerosene range hydrocarbons hydrocracking catalysts are required, whereas for diesel range hydrocarbons less acidic hydrotreating catalysts were needed.

2.4.5.1. Steam reforming

Experimental work confirmed that pyrolysis process can convert lignin to gasoline with reasonable H_2 consumption for mild hydrotreating followed by hydrocracking (Marker *et al.*, 2005). Hydrogen can be produced from a number of sources such as: steam reforming of natural gas; coal gasification; or partial oxidation of hydrocarbons (Y. Zhang, 2014). Steam reforming is a process that produces hydrogen by using the water-soluble phase of pyrolysis oil. The hydrogen production would replace natural gas consumption and could potentially reduce nearly 20% of refinery CO_2 emissions (Marker *et al.*, 2005), but pyrolysis oil yield will drop, because 38% of the entire bio-oil is used for hydrogen production (Wright *et al.*, 2010a; Wright *et al.*, 2010b).

2.4.6. Esterification

A promising option for improving bio-oil quality prior to hydrotreating is esterification (Ciddor *et al.*, 2015). Bio-oil produced from biomass normally has a high oxygen content (20 - 50wt%) and acidity (pH = 2.5 - 3), resulting in a low heating value (16 - 18 MJ/kg), high viscosity and corrosiveness (Milina, Mitchell and Pérez-Ramírez, 2014; Gunawan *et al.*, 2012). Esterification reduces acidity by neutralising carboxylic acids in the bio-oil, which improves stability and reduces catalyst deactivation and hydrogen consumption during hydrotreating (Lohitharn and Shanks, 2009; Miao and Shanks, 2009; Tang *et al.*, 2009; Li *et al.*, 2011a; J. Xu *et al.*, 2011; Milina *et al.*, 2014).

2.4.7. Ketonisation

Another pre-hydrotreating method is ketonisation, which is a condensation reaction that enables the partial reduction of oxygen in the form of water (Milina *et al.*, 2014). Ketonisation is a reaction that transforms two carboxylic acids into ketone, carbon dioxide and water (Renz, 2005; Pham *et al.*, 2013). Ketonisation also removes highly reactive carboxylic groups, by converting acetic acid into acetone, and increases the size of the carbon chains, which increases product stability. Furthermore, acetone can be converted, along with other bio-oil components, into longer chain hydrocarbons through aldol condensation/hydrogenation; this prevents small molecule being lost in the form of light gases (Pham *et al.*, 2013; Pham *et al.*, 2012). Ketonisation can be performed on pyrolysis vapours, but conducting ketonisation on the liquid phase minimises decomposition and re-polymerisation of the bio-oil. Gravity phase separation was

previously used for fast pyrolysis in a fluidised bed reactor (Marker *et al.*, 2005). Phase separation is required to obtain light oxygenates for the ketonisation process, and this can be followed by aldol condensation (Pham *et al.*, 2012). The sugar and lignin derived components can then undergo esterification.

2.5. Definition of the bio-oil upgrading scenarios

This study focuses on converting pyrolysis oil to different transportation fuels by using different upgrading methods based on the previous findings in the literature.

Considering the structural complexity of bio-oil, a synergy of technologies is needed to upgrade bio-oils into synthetic fuels. Therefore, some emerging combinations of pyrolysis and upgrading methods to obtaining sustainable transportation fuels from pyrolysis were further proposed.

Based on the review of the upgrading methods, six alternative scenarios are outlined: i) hydrotreating and hydrocracking; ii) esterification, hydrotreating and hydrocracking; iii) esterification/ketonisation, hydrotreating and hydrocracking; iv) two-stage hydrotreating and hydrocracking; v) esterification, two-stage hydrotreating and hydrocracking, and vi) esterification/ketonisation, two-stage hydrotreating and hydrocracking. Scenarios 1 and 4 have been outlined in numerous studies and several sustainability studies of scenario 1 have been performed by other researchers (Peters, Iribarren and Dufour, 2015; Dang, Yu and Luo, 2014; Y. Zhang, 2014; Iribarren *et al.*, 2012; Snowden-Swan and Male, 2012). A few authors have considered introducing esterification into the upgrading process (scenarios 2 and 5), but the environmental impacts have not been evaluated (Ciddor *et al.*, 2015; Milina *et al.*, 2014). More recently, ketonisation and aldol condensation have been suggested (Milina *et al.*, 2014), and scenarios 3 and 6 are extensions of a process proposed by Pham et al. (2014). Two different ways of obtaining hydrogen were considered: from an external source (produced from natural gas), and produced internally through bio-oil steam reforming. The bio-oil production process and the six upgrading scenarios to be analysed are outlined in Figure 2.11, and their main differences are summarised in Table 2.6.
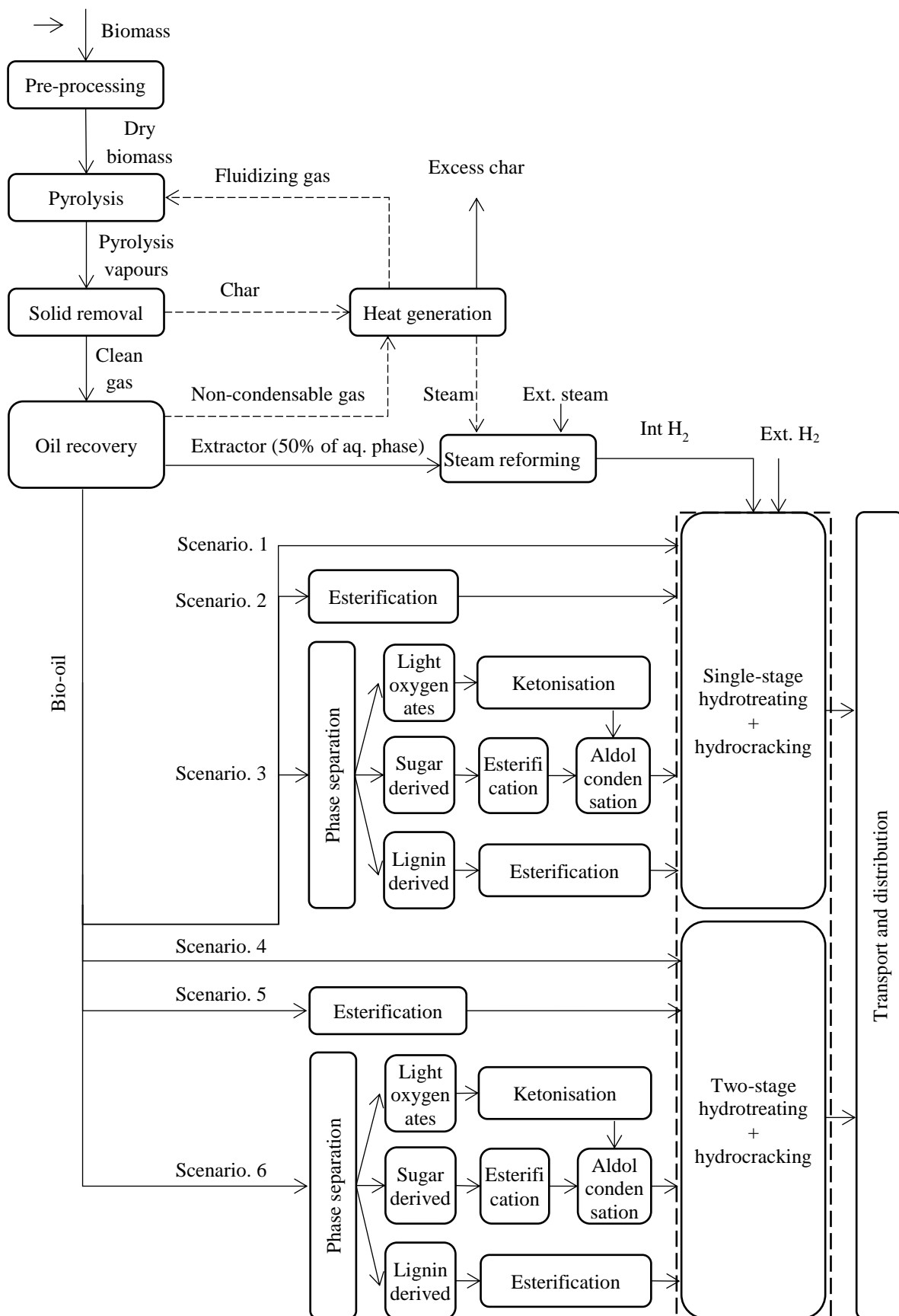
Figure 2.11: Block diagram of biomass fast pyrolysis and upgrading processes

Table 2.6: Summary of the six different bio-oil upgrading scenarios

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 synthetic fuel with a low oxygen and acidic component content.

2.6. Summary

In this chapter, a rigorous literature review was carried out on different methods to convert biomass into bio-oil and upgrade into synthetic transportation fuels. Based on the most appropriate methods of conversion and the lack of knowledge in the field, it was concluded that improving pyrolysis oil properties might be a viable way to produce sustainable transportation fuels of an appropriate specification and six different scenarios for further analysis were identified.

Chapter 3

3. Methodology

3.1. Introduction

This chapter outlines the methodology adopted to evaluate the six scenarios identified within the literature review. To achieve the project's aim of investigating the sustainability of synthetic fuels, a holistic approach is adopted to compare the alternative options with fossil fuels using key environmental, technical and economic indicators. Life cycle assessment was carried out to find the environmental impact of proposed upgrading scenarios. Next, an economic analysis was performed to find the cost of each scenario and the technological performance of each scenario was assumed from literature data. To enable a systematic approach to be taken to compare the scenarios based on the techno-socio-economic data gathered, a series of alternative multi-criteria decision-making methods were applied. An overall output from the decision analysis was a preferential ranking of the scenarios.

3.2. Life cycle assessment

The life cycle assessment (LCA) is a systematic analytical method for identifying, quantifying and evaluating environmental impacts that may occur in all stages of a life cycle, when developing products, processes and services. LCA can therefore evaluate the environmental effects of a product over the entire period of its operating life, and is a tool that supports environmental decision-making. LCA consist of goal and scope definition, inventory analysis, impact assessment and interpretation. The LCA used in this study is based on the ISO 14040 and ISO 14044 series (ISO, 2006b; ISO, 2006a). Chapter 4 carries out an LCA of each pyrolysis oil upgrading scenario in conformance with these ISO standards, see Figure 3.1.
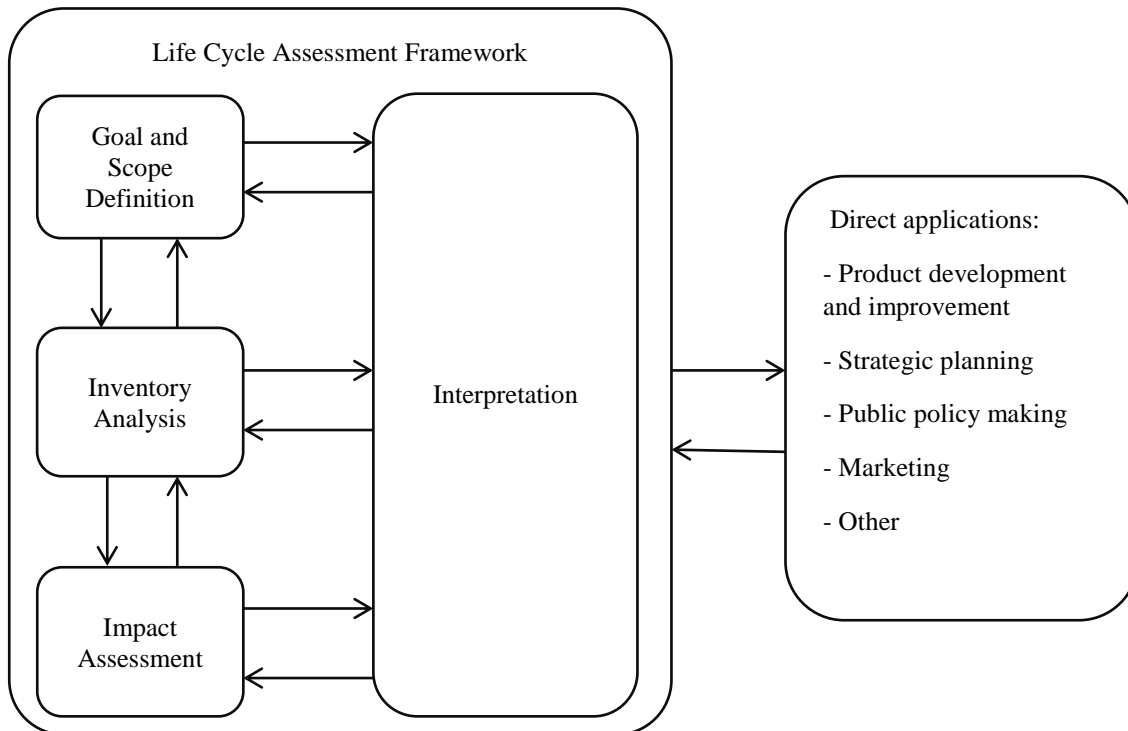
Figure 3.1: Life cycle assessment framework - ISO 14040 (ISO, 2006b)

A life cycle assessment of each scenario was performed using GaBi Professional with the integrated Ecoinvent database. The applications for GaBi Software are various, for example it can aid the design of products with low environmental impact, reduce wastage or develop profiles of carbon and other products' environmental footprints. The GaBi databases are derived from industry sources, scientific knowledge, technical literature, and internal patent information – creating a solid foundation for assessing materials, products, processes and services. The Ecoinvent database can be fully integrated in the GaBi software and provides access to unit processes and inventories for a wide range of different industrial areas (GaBi, 2018). A well-to-wheel analysis was adopted to consider all the resource inputs and outputs from biomass cultivation to fuel combustion in a vehicle. The LCA system boundary also includes biomass transportation, biomass preparation, an integrated bio-oil production and upgrading plant, and fuel transportation (see Figure 3.2). The functional unit used to compare the alternative scenarios is one kilogram of upgraded fuel. One mega joule of energy content of the upgraded fuel is not used due to the uncertainties of fuel quality in certain scenarios, but conversions are made where data is available.
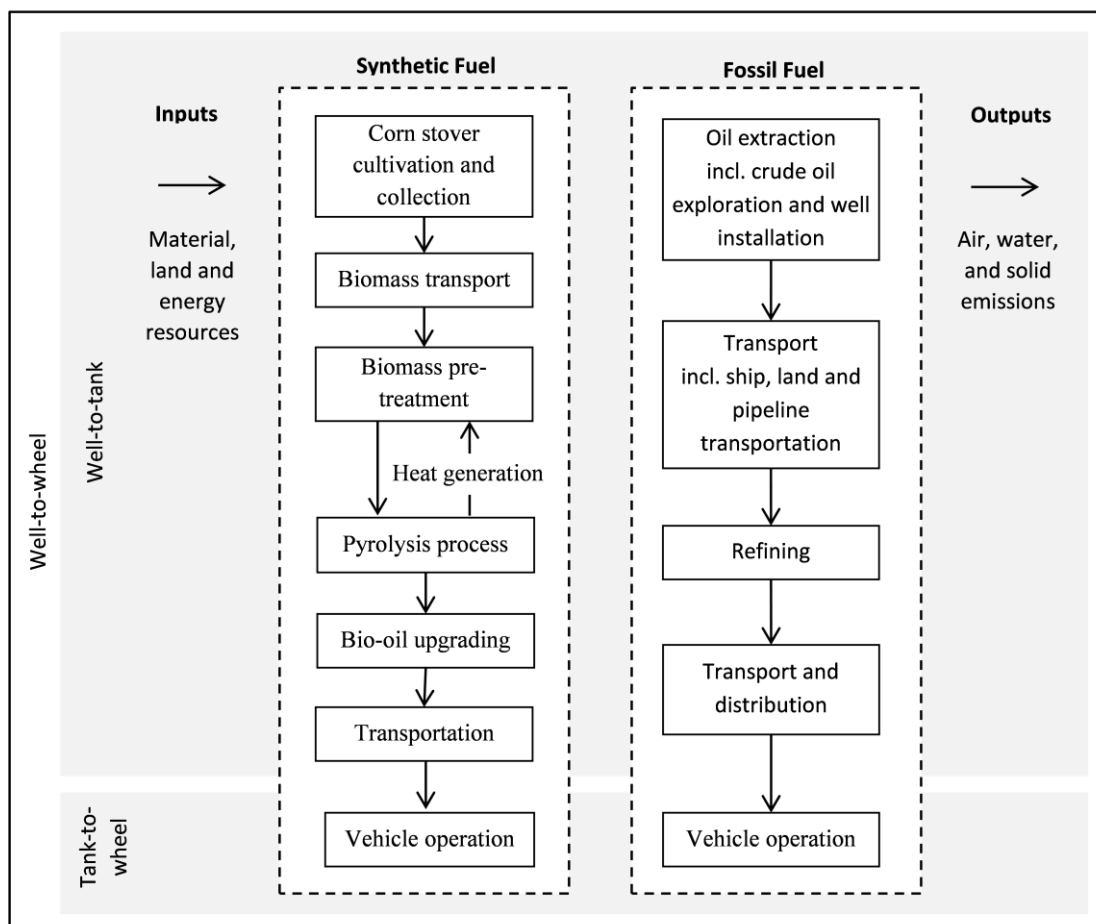
Figure 3.2: Life cycle system boundary for the production of synthetic fuels via fast pyrolysis

To enable the alternative upgrading scenarios to be compared, a fixed feedstock and pyrolysis processing technology was considered throughout. Corn stover was used as it has been considered as a suitable waste feedstock for pyrolysis in a range of studies (Dang *et al.*, 2014; Y. Zhang, 2014). The fluidised bed reactor operating under fast pyrolysis conditions was considered as it is a popular option due to its ease of operation, high stability under pyrolysis conditions and high oil yields (Bridgwater, 2012b; Jahirul *et al.*, 2012; Ringer, Putsche and Scahill, 2006).

Assessing the environmental impacts of obtaining fuel from residual stover waste is challenging as different allocation methods can have a significant impact on the LCA results. Previous researches on corn stover have had a tendency to use subdivision to avoid allocation to corn grain and subsequent co-products (Murphy and Kendall, 2013). The LCA configuration assumes changes to an existing continuous corn production

system and assigns additional processes for the collection and nutrient replacement of partially gathered stover, which would have otherwise been left unharvested. Subdivision of the co-products arising in each scenario is difficult due to the lack of data and established practices with using pyrolysis products and synthetic fuels. Methods adopted in previous studies include no allocation to the by-products — due to the large uncertainties — and mass-, energy- and value- based approaches (Kendall and Chang, 2009; Larson, 2006). In this study, the total energy and material inputs consumed in the production of by-products were included. Where possible, the by-products are used within the system (e.g. heat generation from the pyrolysis gases). Displacement of energy, had the production of the by-products been made via other routes and their market worth, was not considered, which could significantly impact the results. For example, by-products of corn stover, hydrogen and ethanol products were not considered, as it was assumed they were used for other purposes; but further studies may analyse them to establish in what proportion the system's reliability might be affected.

Due to the large uncertainties, where possible, minimum, expected and maximum values were obtained for each stage of the LCA analysis from the literature, GaBi Professional databases and Ecoinvent 3.3. This allowed the most likely values and possible ranges to be obtained in terms of the environmental impacts of each upgrading stage. The sensitivity of the results based on fertiliser and hydrogen usage were further examined, including different sources of hydrogen being modeled. The global warming potential (GWP) of each processing stage and utilised resource was investigated and other environmental impact categories were evaluated based on the CML2001 impact assessment method (Guinée, 2002). These other impacts include, but are not limited to, acidification and eutrophication potential.

The GWP in CO_2-eq was calculated considering the CO_2 direct effect produced through the absorption of infrared radiation and the indirect effect on overall radiation. The acidification potential describes the acidifying effect of substances (ability to form H^+ ions) and was calculated considering the sulphur dioxide (SO_2) and other acidifying substances as S^-, N^- and halogen atoms, measured in SO_2-eq. Soil and water acidification may occur due to transformation of the air pollutants into acids. The eutrophication potential (or nitrification of land and water) can alter the balance

between species and can lead to serious damage in biological populations; and the toxic effect must also be considered. The main substances causing eutrophication are phosphorous (P) and nitrogen (N), and is measured in PO_4^{3-} (phosphate) eq. in this study. The eutrophication often occurs due to fertilisers usage (GaBi, 2016; European Commission, 2005). Other factors, such as: ozone layer depletion, abiotic depletion, human toxicity and ecotoxicity potential (CML2001) were also investigated.

3.3. Economic analysis

To carry out an economic analysis, a range of financial indicators were used. To establish these capital costs (one time fixed expenses, e.g. equipment costs) and operational costs (on-going expenses to maintain commercial existence, e.g. raw materials costs) were calculated for each scenario. The minimum selling price of synthetic fuel produced from each scenario was calculated based on the expected costs (capital and operational costs), the on-stream factor, working capital cost, income tax rate and internal rate of return. The on-stream factor is a productivity unit showing how much time the unit functioned each year (normally referred to as 'availability'). Working capital cost refers to the cost to maintain daily operation within the unit. The internal rate of return is a unit to estimate the profitability of potential investments. It is typically used to derive the discount rate that brings the net present values (NPV) of all cash flows of a system equal to zero. The economic aspect of each technology used in the life cycle assessment scenarios was evaluated and the total cost of each of the six scenario was obtained; two different paths of obtaining hydrogen were considered for all scenarios.

Fixed capital investment (FCI) includes all the assets and capital investments. The FCI of a plant with an assumed capacity of 2000 dry ton of corn stover per day was calculated assuming it was the nth plant (mature technology), normally referred to as n[th] of a kind (NOAK), as opposed to the First of a Kind (FOAK). This therefore assumes that cost and operating efficiencies have been identified based on experience with this type of infrastructure. The capital cost for pyrolysis, hydrotreating and hydrocracking units were found from literature sources. This study used data from Jones et al. (2009), Wright et al. (2010b), Jones et al. (2013) and Zhang et al. (2013) – with reference values scaled to a 2000 tpd plant. In all these sources the equipment was sized using CHEMCAD or Aspen Plus and the equipment cost was obtained by using specific

software (e.g. Aspen Icarus, Aspen Capital Cost Estimator and Aspen Economic Evaluation) for the sized equipment. The FCI costs of esterification and ketonisation were calculated based on Zhang et al. (2013) capital cost estimation for a nth plant formulas, on costs obtained through online estimations (Alibaba.com, 2018). The total capital cost of one kilogram of synthetic fuel produced was then calculated for all six scenarios.

The operational cost of each process was calculated based on raw materials costs (corn stover), utilities costs (electricity, process water) and operating material costs (catalysts, ethanol, waste disposal); the steam was assumed to be produced in the system and the fixed operational costs, such as salaries and maintenance were taken from literature review. Using all this data the total operational cost of one kilogram of synthetic fuel produced was then calculated for all six scenarios.

The minimum, expected and maximum costs to produce one kilogram of synthetic fuel for each scenario were calculated by using all the inventory data for capital and operational costs.

The minimum fuel product selling price (MFSP) for the synthetic fuel was determined using a discounted cash flow rate of return analysis. The methodology is similar to that used in Jones et al. (2009), (2013) and Zhang et al. (2013). A sensitivity analysis was carried out to examine the effect of different financial and operating assumptions on the MFSP.

3.3.1. The Financial model

The financial model was built using previous techno-economic studies (S. Jones *et al.*, 2013; S. B. Jones *et al.*, 2009; Y. Zhang *et al.*, 2013)

3.3.1.1. Capital cost per kilogram of synthetic fuel produced for each scenario

The total capital cost (Tcc) was obtained by summing up the capital cost of each process (Pc). The total capital cost also included the maintenance, insurance and tax fees.

$$Tcc= \sum_1^n (Pc) \; ; 1, …, n – \text{the processes involved in each scenario} \qquad (1)$$

Next, the capital cost to be paid for each year (CCy) was assumed to be the total capital cost divided by the period of time to pay back the debt (DFy) – which was assumed to be 10 years.

$$CCy \; [\$] = \frac{Tcc}{DFy} \; [\$ / \text{ year}] \tag{2}$$

The capital cost per day (CCd) was calculated by dividing the capital cost of each year by the on-stream factor (SF). The on-stream factor was assumed to be 350 days per year.

$$CCd \; [\$] = \frac{CCy}{SF} \; [\$ / \text{ days}] \tag{3}$$

The capital cost for each kilogram of biomass (CCbm) was calculated by dividing the capital cost per day to the number of kilogram processed each day (BP). For this study, it was assumed to process 2.000.000 kg of feedstock per day.

$$CCbm \; [\$] = \frac{CCd}{BP} \; [\$ / \text{ kg biomass}] \tag{4}$$

Finally, the capital cost per kg of synthetic fuel was found by multiplying the capital cost for each kilogram of biomass with the number of kilograms needed to obtain one kilogram of synthetic fuel (BN).

$$CCbf \; [\$] = CCbm \; \text{x} \; BN \; (kg) \; [\$ / \text{ kg synthetic fuel}] \tag{5}$$

3.3.1.2. Operational cost per kilogram of synthetic fuel produced for each scenario

Operational cost per kilogram of synthetic fuel (OCbf) was calculated by summing up the materials involved in all the technologies needed to produce one kilogram of synthetic fuel (for each scenario). The material cost (MCbf) for each element involved in each process was calculated by multiplying the cost of one kilogram of material (MC) with the material quantity (MQ) involved in the process.

$$MCbf \; [\$] = MC \; (\$ / \text{ kg}) \; \text{x} \; MQ \; (kg) \tag{6}$$

$$OCbf \; [\$] = \sum_1^m (MCbf) \; ; 1, \ldots, m - \text{ the materials involved in each scenario} \tag{7}$$

3.3.1.3. Total cost per kilogram of synthetic fuel produced for each scenario

The debt capital cost per kilogram of synthetic fuel (CCdbf) is equal to the capital cost of one kg of synthetic fuel (CCbf) summed with the interest rate of debt financing (IRB).

CCdbf [$] = CCbf [$] + IRB [%]   (8)

The total cost (TC) is equal to the sum of OCbf with CCdbf.

TC [$] = OCbf [$] + CCdbf [$]   (9)

The minimum selling price of one kilogram of synthetic fuel is equal to the total cost of one kilogram of synthetic fuel multiplied by the working capital cost (WCC) (including land) and the internal rate of return (IRR), and gathered with the income tax rate (ITR). WCC is responsible for maintaining daily operation & short term debt; IRR is the possible profit of the company, and ITR is imposed by the federal government.

MSP [$] = TC [$] x WCC [%] x IRR [%] + ITR [%]   (10)

where WCC and IRR are fixed values

and ITR = V [%] x IRR (V – fixed value)

After the total production cost per kilogram of synthetic fuel was found, the sensitivity analysis was conducted by varying some of the factors one by one (main operational costs, operational period of time, the income tax rate, working capital costs and internal rate of return), to determine how independent factors affect the total cost.

3.4. Multi-criteria decision-making (MCDM)

3.4.1 Identify the goal and select the criteria, sub-criteria and alternatives

Multiple-criteria decision-making (MCDM) refers to making decisions in the presence of multiple, usually conflicting, criteria (L. Xu and Yang, 2001). The goal of the MCDM system in this study was to find the best scenario for producing transportation fuels. The criteria and sub-criteria were chosen to be aligned with the decision to be made, independent of each other and measurable (Majumder, 2015). Therefore, the

criteria were represented by Environment, Economical and Technical criteria and the sub-criteria were represented by the main factors that affected each criterion and quantified importance by means of a survey. The existing alternatives must be comparable and feasible (Majumder, 2015), and in this circumstance they were represented by the six pyrolysis oil upgrading scenarios (see Section 2.5).

3.4.1.1. Choosing the sub-criteria

Although there are numerous environmental impacts (Vienescu *et al.*, 2017) that need to be considered when evaluating upgraded bio-fuels, global warming potential, acidification potential and eutrophication potential were chosen as environmental sub-criteria for the MCDM study.

Considering the necessity to improve biofuel quality, the main technical sub-criteria selected for specific analysis were oxygen content, acidity and viscosity. The economic sub-criteria were chosen to be the main cost constituents: the capital cost, the operational cost and the minimum selling price.

Decision-making is an important factor in the production of synthetic fuels. Therefore, the decision criteria and goals are to minimise: Global warming potential (GWP), Acidification (AP), Eutrophication (EP), Capital cost, Operational cost, Minimum selling price, Oxygen content, Viscosity and Acidity.

3.4.2. AHP and TOPSIS

From the various MCDM methods AHP and TOPSIS were found to be the most utilised ones (Mardani *et al.*, 2015). The AHP method was developed by Satty (1987) to model subjective decision-making processes. TOPSIS is a decision-making process based on an objective weighting method. TOPSIS is a multi-criteria analysis method that compares a set of alternatives and chooses the alternative with the smallest deviation from an ideal solution and furthest from the negative ideal solution (J. Wang *et al.*, 2009; Assari, Mahesh and Assari, 2012).

For this study the AHP and TOPSIS methods were chosen to be the most appropriate multi-criteria decision-making analysis methods. The combined (compromised) method

between entropy (Zou, Yi and Sun, 2006; Li *et al.*, 2011b; Çalışkan *et al.*, 2013) and AHP methods (J. Wang *et al.*, 2009; Çalışkan *et al.*, 2013) were used to get the most appropriate weighting of each criterion. The entropy measures the uncertainty in the information by using probability theory, considering that a broad distribution represents more uncertainty than a narrow one (Rao, 2007).

3.4.2.1. AHP Method

The alternatives being compared against each criteria and sub-criteria using the AHP framework are shown in Figure 3.3.
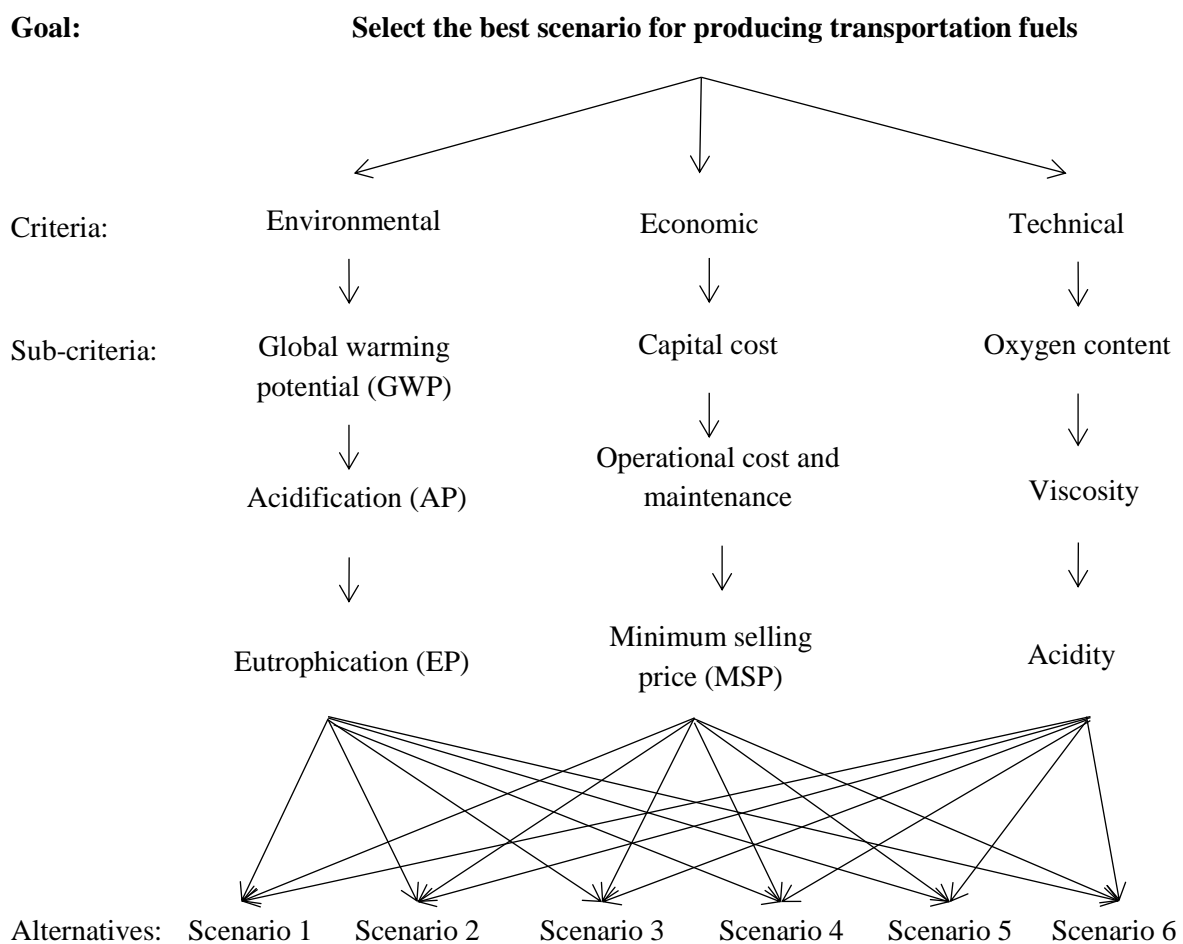
Figure 3.3: AHP – hierarchical framework for producing transportation synthetic fuels

The AHP method uses pair-wise comparisons to compare the criteria and calculate the criteria weights; this establishes the difference in importance of each sub-criteria in relation to the goal of the analysis. The weightings coefficients and pair-wise comparisons typically use data gathered from experts using surveys. Even if there is a variation in the input data obtained from questionnaires, the criteria weighting can still

be reliably obtained (Leung *et al.*, 1998). In this study, three experts with industrial and academic backgrounds on pyrolytic processes were used to quantify the importance of the chosen criteria and sub-criteria. The survey was sent to 25 experts in the field, so a participation rate of 12% was achieved, which included experts from the UK and USA working in bioenergy research centers. The participants information is not disclosed as consent was not obtained. As the number and type of chosen experts can influence any MCDM results, a sensitivity study was performed to investigate how this might change the results.

A fundamental scale for pair-wise comparisons was used in the questionnaire to assess the intensity of preference between two elements. The scale contained values from 1 to 9: 1 indicating equal importance, 3 indicating moderate importance, 5 indicating strong importance, 7 indicating very strong importance and 9 indicating extreme importance. Intensities of 2, 4, 6 and 8 were used to express intermediate values. Intensities of 1.1, 1.2, 1.3, etc. can be used for elements that are very close in importance, but were not used in this study.

A matrix A was creating by recording the numerical judgments a_{ij}, as below:

$$A = \begin{bmatrix} a_{11} & \cdots & a_{1j} & \cdots & a_{1n} \\ \vdots & & \vdots & & \vdots \\ a_{i1} & \cdots & a_{ij} & \cdots & a_{in} \\ \vdots & & \vdots & & \vdots \\ a_{n1} & \cdots & a_{nj} & \cdots & a_{nn} \end{bmatrix}, a_{ii} = 1, a_{ij} = 1/a_{ji}, a_{ji} \neq 0, i, j = 1, 2, \ldots, n \qquad (1)$$

The numerical weights were extracted, resulting in weight vectors:

$W = (W1, W2, \ldots, Wn)$ $\qquad (2)$

where W is the principal eigenvector of the matrix A and

$AW = \lambda_{max} W$, where λ_{max} is the principal eigenvalue of matrix A $\qquad (3)$

Because it it possible for users to provide conflicting answers in their perceptions, the model consistency has to be verified. This was calculated based on a consistency index (CI) and random consistency index (RI) to determine a consistency ratio (CR). The model was considered to have an acceptable level of inconsistency if the resulting consistency ratio was less than or equal to 10% (Saaty 1990).

$$CI = (\lambda_{max} - n) / (n - 1) \text{, where n is the size of the matrix} \tag{4}$$

$$CR = CI / RI \tag{5}$$

3.4.2.2. TOPSIS Method

For the TOPSIS method, the criteria weighting are the same as for AHP; however, the performance of the alternatives against each criteria are assessed differently, by considering the deviation from an ideal solution. The MCDM framework using TOPSIS method is outlined in Figure 3.4. See an example of TOPSIS methodology in Appendix1.
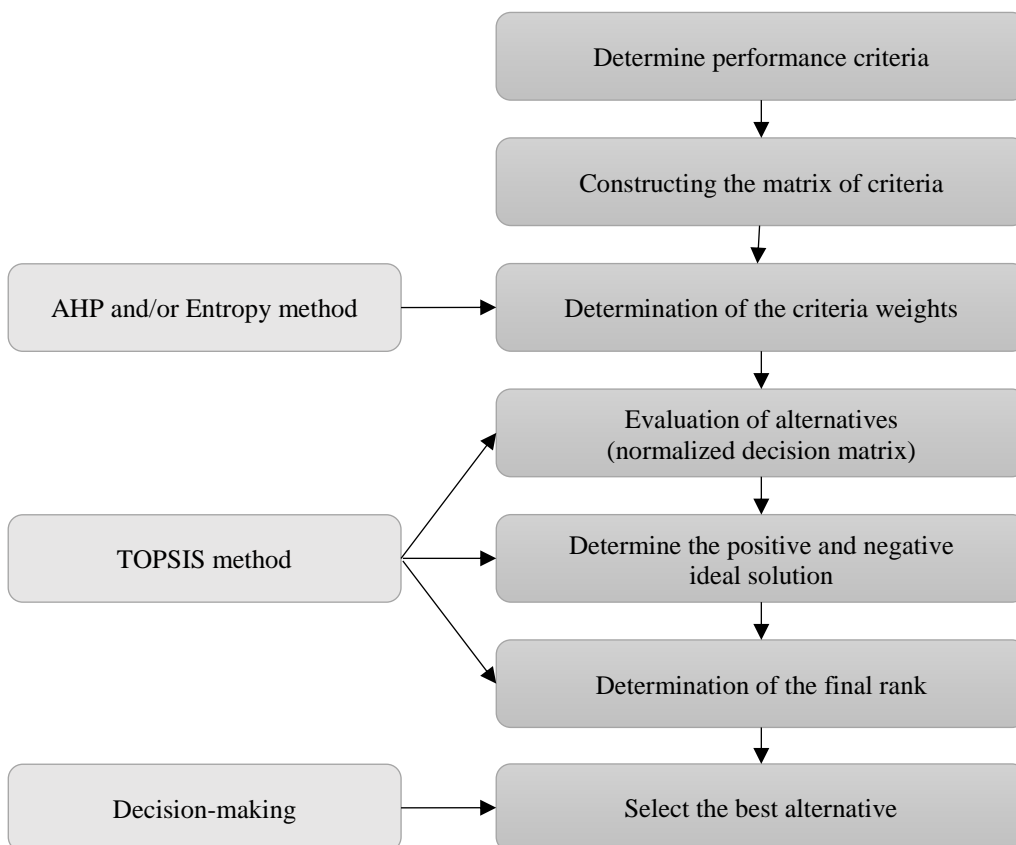
Figure 3.4: MCDM using TOPSIS method

3.4.2.2.1. TOPSIS Steps

The TOPSIS method comprises the following steps (Shanian and Savadogo, 2006; Roszkowska, 2011):

Step 1: Construct the decision matrix and determine the criteria weights

Construct the decision matrix consisting of *m* alternatives and *n* criteria. Considering that the intersection of each alternative and criteria is given as a_{ij}, results in a matrix A= $(a_{ij})_{mxn}$.

Selecting the criteria weights can be done by using AHP, entropy or compromised methods:

1.1. Entropy Method (Qiu, 2002; Zou *et al.*, 2006)

Normalisation of the data to get R = $(r_{ij})_{mxn}$; where, r_{ij} is the data of the *i*th evaluating object on the criteria, and $r_{ij} \in [0,l]$.

Criteria can be divided into: more is better, for example benefit criteria; and less is better, for example cost criteria. Among these criteria, where the bigger is better are calculated by:

$$r_{ij} = \frac{aij - min_j\{aij\}}{max_i\{aij\} - min_i\{aij\}} \tag{6}$$

where the smaller is better are calculated by:

$$r_{ij} = \frac{max_j\{aij\} - aij}{max_i\{aij\} - min_i\{aij\}} \tag{7}$$

The entropy value E_j of *j*th criteria can be defined as:

$$E_j = \frac{\sum_1^m fij\ \ln(fij)}{\ln m}\ , (i = 1, \dots, m;\ j = 1, \dots, n) \tag{8}$$

where $f_{ij} = \frac{rij}{\sum_{i=1}^m rij}\ , (i = 1, \dots, m;\ j = 1, \dots, n)$

The weight of the entropy of *j*th criteria can be determined by:

$$w_j = \frac{1 - E_j}{n - \sum_{j=1}^n E_j}\ , \sum_{j=1}^n w_j = 1, 0 \le w_j \le 1, (j = 1, \dots, n), \tag{9}$$

1.2. Compromised (combined) Method (Chu and Su, 2012)

To achieve the compromised (combined) weightings, the AHP and entropy methods can be combined, in order to consider the subjective and objective weights of the criteria and to obtain more realistic weight coefficients.

The compromised weight for the *j*th criteria is:

$$w_j = \frac{\alpha_j \times \beta_j}{\sum_{j=1}^{n}(\alpha_j \times \beta_j)} \; , j = 1, \ldots, n \tag{10}$$

Step 2: Calculate the normalised decision matrix

The matrix $A = (a_{ij})_{mxn}$ is then normalised, to convert all attribute dimensions into non-dimensional attributes, to form the matrix $R = (r_{ij})_{mxn}$, using the normalisation method. The normalization must be performed because various criteria are measured in different units, and the data must be converted to a normalised scale.

$$r_{ij} = \frac{a_{ij}}{\sqrt{\sum_{i=1}^{m} a_{ij}^2}} , \; i = 1, 2, \ldots, m; j = 1, 2, \ldots, n \tag{11}$$

Step 3: Calculate the weighted normalised decision matrix

The weighted normalised value t_{ij} is calculated by multiplying the columns of the normalised decision matrix by the associated weights:

$$t_{ij} = r_{ij} * w_j , \; i = 1, 2, \ldots, m; j = 1, 2, \ldots, n \tag{12}$$

where *wj* is the weight of *j*th criterion: $w_j = \frac{W_j}{\sum_{j=1}^{n} W_j}$, $j = 1, 2, \ldots, n$; so that $\sum_{j=1}^{n} w_j = 1$

Step 4: Determine the best alternative A_b and the worst alternative A_w

The best alternative (positive ideal alternative) maximises the benefit criteria and minimises the cost criteria, and the worst alternative (negative ideal alternative) maximises the cost criteria and minimises the benefit criteria.

Positive ideal solution A_b has the form:

$$A_b = (t_{b1}, t_{b2}, \ldots, t_{bn}) = \{[\max_i t_{ij} | j \in I], \min_i t_{ij} | j \in J]\} \tag{13}$$

Negative ideal solution A_w has the form:

$$A_w = (t_{w1}, t_{w2}, \ldots, t_{wn}) = \{[\min_i t_{ij} | j \in I], \max_i t_{ij} | j \in J]\} \tag{14}$$

where I is set for the criteria having a positive impact, and J is set for the criteria having a negative impact; and $i = 1, 2, \ldots, m$, $j = 1, 2, \ldots, n$.

Step 5: Measure distance from the positive ideal solution and the negative ideal solution

The distance between the target alternative *i* and the best condition A_b is calculated by:

$$d_{ib} = \sqrt{(\sum_{j=1}^{n}(t_{ij} - t_{bj})^2)^{1/2}} \; ; i = 1, 2, \ldots, m \tag{15}$$

and the distance between the target alternative i and the worst condition A_b is calculated by:

$$d_{iw} = \sqrt{(\sum_{j=1}^{n}(t_{ij} - t_{wj})^2)^{1/2}} \; ; i = 1, 2,\ldots,m \tag{16}$$

where d_{ib} and d_{iw} are L2-norm (Euclidian) distances from the target alternative i to the best and worst conditions, respectively.

Step 6: Calculate the similarity to the ideal condition

The relative closeness to the positive ideal condition, Ci, can be calculated as:

$$C_i = d_{iW} / (d_{iW} + d_{ib}) , \; 0 \leq C_i \leq 1; i = 1, 2,\ldots,m \tag{17}$$

Step 7: Rank the preference order or select the alternative closest to 1

The higher the closeness means a higher rank. The alternatives can be ranked by the descending order of the value of C_i ($i = 1, 2,\ldots,m$).

3.4.3. Aggregation method

The aggregation method was used to find the final ranking from all three methods used in this study: AHP, TOPSIS with entropy weightings (EW) and TOPSIS with compromised weightings (CW). A very general method to obtain the final ranking is the voting method. Depending on the rule used, two different voting methods can be used: Borda and Coperland (Conitzer, 2006). The Borda rule assigns points for each alternative and selects the option that on average stands highest in points. It assigns points for the m alternatives, the top ranked alternative has m-1 points, second ranked alternatives have m-2 points, and the bottom ranked alternative has 0 points. Finally, the alternatives are ranked according to the average number of points, the best option being the one with the highest number of points. The Coperland rule uses pair-wise comparisons to select the alternatives which beat each other and find the best option. It calculates for each alternative, how many alternatives does it beat and how many does it lose against, from the total number of alternatives. The difference between these two values is then calculated. Finally, the alternatives are ranked according to the highest value, with the best option being the one with the peak value.

A thesis methodology diagram, with the steps followed to find the best option to produce sustainable synthetic fuels, is outlined next in Figure 3.5.
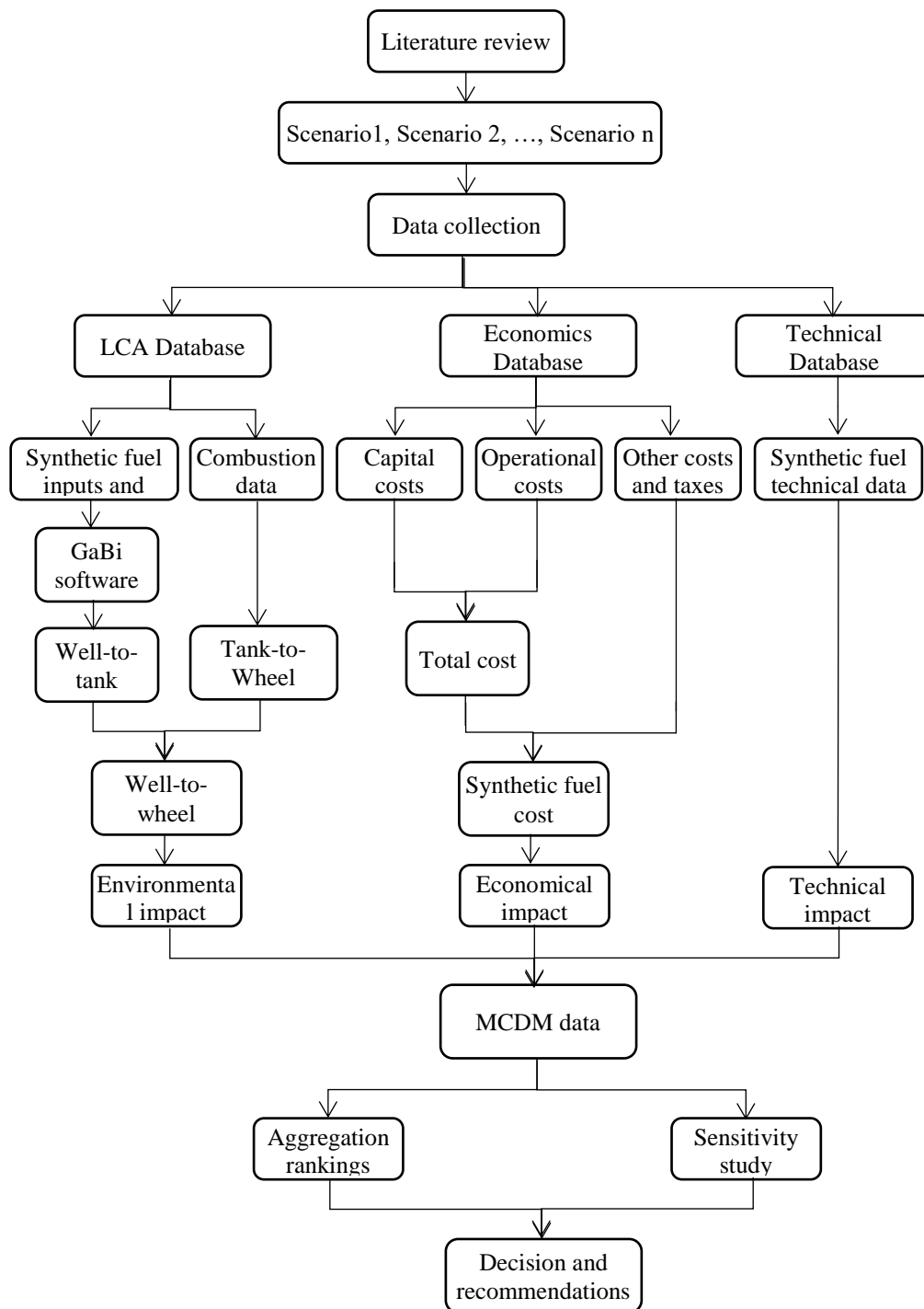
Figure 3.5: Methodology diagram

3.5. Summary

The methodology chapter outlined the methods used to analyse sustainable production of synthetic fuels from waste biomass by using different technologies. Six different scenarios were designed by using the existing and proposed technology synergies (see Section 2.5) and were considered to be the alternatives for the MCDM system. Specific environmental, economic and technical parameters were considered to be the criteria to be analysed using AHP and TOPSIS methods in order to find which alternative is the most suitable scenario for the production of sustainable synthetic fuel.

Chapter 4

4. Life Cycle Assessment of the Production of Synthetic Transportation Fuels Using Different Systems

4.1. Introduction

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) (Blakey, Rye and Wilson, 2011). LCA enables comparisons to be made with fossil fuels and other technological options for producing bio-fuels.

A number of LCA studies on fuels obtained from pyrolysis and other thermochemical conversion processes have been carried out by researchers. Iribarren *et al.* (2012) conducted a life cycle assessment of pyrolysis coupled with hydrotreating. Seven environmental impact categories were considered: global warming, cumulative energy demand, ozone layer depletion, land competition, photochemical oxidant formation, acidification and eutrophication. They concluded that the highest impacts were associated with the use of electricity for feedstock processing and natural gas for obtaining hydrogen through steam reforming. Snowden-Swan and Male (2012) conducted a study on pyrolysis with hydrotreating upgrading of poplar residues and they found the GHG emissions to be in the order of 32.5 gCO_{2-e}/ MJ. Peters *et al.* (2015) simulated a pyrolysis plant and biorefinery for fast pyrolysis of hybrid poplar. An LCA analysis was then conducted to see which of the processes of hydrotreating, hydrocracking, distillation or steam reforming had the most negative environmental impact. They found that the key contributors for GHG emissions were the pyrolysis plant and the biorefinery, with a total of 40 gCO_{2-eq}/ MJ, suggesting that the environmental impact could be improved by seeking ways to reduce the electricity consumption.

Dang et al. (2014) used LCA to compare three different ways of upgrading corn stover bio-oil into transportation biofuels. The first case considered using hydrogen from external natural gas reforming. The second case considered producing hydrogen inside the plant using 35% of the bio-oil aqueous phase, and the third option considered producing a surplus of hydrogen using the entire bio-oil aqueous phase. The GHG emissions were respectively 50 gCO_{2-eq}/ MJ, 70 gCO_{2-eq}/ MJ and 180 gCO_{2-eq}/ MJ. Zhang (2014) also looked into how the hydrogen used in the upgrading of fast pyrolysis bio-oil (from corn stover) to biofuel impacts the environment. The LCA study gave similar GHG emission results of approximately 40 gCO_{2-eq}/ MJ. In comparison, conventional transportation emits around 94 CO_{2-eq}/ MJ. Swan et al. (Snowden-Swan and Male, 2012) 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_2 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. (Hsu, 2012) conducted a life cycle assessment of gasoline and diesel produced through fast pyrolysis and hydroprocessing; it showed that hydroprocessing made a significant contribution to the total CO_2 emissions: around 55% in diesel production and 60% in gasoline production.

Hydrogen can be obtained from different sources, but large scale hydrogen production tends to be achieved through steam reforming of natural gas (methane) (Kothari, Buddhi and Sawhney, 2008). However, due to natural resources usage to produce hydrogen, some authors suggested producing hydrogen internally, through steam reforming of pyrolysis bio-oil aqueous phase (Marker *et al.*, 2005; C. Yan, Cheng and Hu, 2010).

Several authors have used LCA to investigate the environmental impacts of producing fuels from pyrolysis. Irribaren et al. (2012) conducted a life cycle assessment of pyrolysis of poplar followed by hydrotreating, and found that over 40% of the total CO_2 emissions result from using steam reforming to obtain hydrogen. Peters et al. (2015) simulated a pyrolysis plant and biorefinery (hydrotreating, hydrocracking, distillation and steam reforming) for fast pyrolysis of hybrid poplar and hydro-upgrading. It was found that the energy demand from steam reforming natural gas was 30% of the total energy demand of producing and upgraded biofuels. Reducing electricity consumption

was considered one of the key factors in reducing the overall environmental impact. Swan et al. (Snowden-Swan and Male, 2012) looked into biomass conversion to biofuels through pyrolysis and upgrading (hydro treatment and hydrocracking) where hydrogen was produced through steam reforming; the conversion accounted for 63% from the total CO_2 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 (Hsu, 2012) 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_2 emissions: around 55% in diesel production and 60% in gasoline production. Dang et al. (2014) carried out a life cycle assessment of bio-fuel production from corn stover feedstock focusing on the GHC 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 (Dang *et al.*, 2014; Iribarren *et al.*, 2012; Snowden-Swan and Male, 2012; Peters *et al.*, 2015; Hsu, 2012). Only a few take into consideration hydrocracking or other upgrading methods (Snowden-Swan and Male, 2012; Peters *et al.*, 2015). 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 benefits in comparison to fossil fuels.

The majority of LCA studies on bio-fuels obtained from pyrolysis have focused on considering pyrolysis with hydroprocessing (Peters *et al.*, 2015; Dang *et al.*, 2014; Y. Zhang, 2014; Iribarren *et al.*, 2012; Snowden-Swan and Male, 2012). However, the structural complexity of bio-oil makes it difficult to find a single comprehensive upgrading method; therefore, there is a rising interest in using a synergy of technologies (Dickerson and Soria, 2013). However, there are many upgrading options and additional processing stages, which must be considered if fuels of a comparable quality to fossil fuels are to be obtained. It is also difficult to compare LCA studies that have considered different upgrading methods. The assumptions made among studies vary, such as the feedstock type, pyrolysis technology and processing condition (slow, fast, intermediate).

LCA results are also highly subjective and variable, and there is often a lack of transparency with the data used. This chapter, therefore, aims to analyse the environmental impacts of the main emerging bio-oil upgrading technologies, so that a more informed comparison can be made to guide future R&D on obtaining synthetic fuel from pyrolysis. Moreover, the possible range in LCA data needs to be investigated to highlight the sensitivity of the results. This will enable a combination of pyrolysis and upgrading methods to be identified, which give good fuel yields and quality, whilst still offering environmental benefits in comparison to fossil fuels.

The following section is based on the method outlined in the Methodology Chapter and the pyrolysis upgrading scenarios defined in Figure 2.11 (see Section 2.5). Gathered LCA inventory data, including possible ranges in values, are presented in Inventory data section, and the LCA results are outlined and discussed in further sections.

4.2. Inventory analysis

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

4.2.1. Feedstock collection, transport and pre-treatment

The inventory data associated with corn cultivation depends on the assumed soil conditions and anticipated crop yields (see Table 4.1). The majority of corn fields are treated with fertiliser to meet the high demand of nitrogen, phosphate and potassium in corn cultivation, and additional requirements are needed when corn stover is removed. Crop rotation is not considered, which could reduce these requirements. Most LCA studies on corn stover use an allocation approach based on nutrient replacement, with stover comprising 0.8% N, 0.2% P_2O_5, and 1.45% K_2O. For a crop yield of 147 bushels/acre, 1.6 dry tons/acre of stover can be sustainably gathered, as a stover collection rate of 40% is considered suitable to avoid soil quality degradation (Murphy and Kendall, 2013). Annual fertiliser application rates are determined based on common fertiliser nutrient composition: ammonium phosphate nitrate (8% N, 52% P_2O_5), ammonium nitrate (35% N) and potassium chloride (60% K_2O). Field emissions arising from the denitrification process by soil micro-organisms are taken as 1.25% g N_2O/ g N: all the emissions allocated to K, N and P are provided in Nemecek et al. (2007).

Direct land use change emissions depend on soil characteristic baseline assumptions. Carbon stored in soil can be released during field preparations or sequestered in degraded soils; however, stover removal is expected to reduce potential carbon sequestration. Most studies do not include land change emissions, assuming existing corn cropland would be used for gathering stover land (Larson, 2006); however, land emissions could have a significant impact and should be considered in specific site evaluations.

The energy requirement for cutting, baling, field transport and on-site storage of the stover has been reported to range from 0.22 (Dang *et al.*, 2014) to 0.83 MJ/kg of stover (Murphy and Kendall, 2013). This study assumes that this demand would be met with diesel fuel. The grain is not considered within the system boundary and therefore the additional fertiliser and energy requirements for gathering corn grain are not included. However, further studies may analyse the by-products to find in what proportion the system's reliability can be affected.

Table 4.1: Model inputs and outputs for the collection of corn stover

Item	Min	Exp	Max	Unit
Inputs				
Fossil energy	0.22	0.53	0.83	MJ/kg of corn stover
Ammonium nitrate phosphate, as P_2O_5		2		g/kg of corn stover
Potassium chloride, as K_2O		14.5		g/kg of corn stover
Ammonium nitrate, as N		8		g/kg of corn stover
Outputs				
Collected corn stover		1		kg

Subsequent transportation would be required to take the raw feedstock from collection point to the bio-oil production plant (see Table 4.2). The transportation distance is assumed to range from 50 - 100 km, with 75 km being the most likely value (Y. Zhang, 2014; Dang *et al.*, 2014; Han *et al.*, 2013). A 9.3 t payload truck from the GaBi Professional database has been used to meet this transportation requirement, which is equivalent to minimum expected and maximum diesel usage of 0.05, 0.075 and 0.1 MJ/kg of delivered corn stover, respectively (GaBi, 2017).

Table 4.2: Biomass collection and distribution

Item	Min	Exp	Max	Unit
Inputs				
Diesel	0.05	0.075	0.1	MJ/kg of delivered corn stover
Outputs				
Biomass		1		kg

Pre-treatment of the feedstock prior to pyrolysis involves grinding and drying to reduce particle size and moisture content (see Table 4.3). Mechanical feedstock size reduction is required because fluidised bed reactors are designed to use small particles ranging from 2 - 3 mm. The expected energy for grinding and chopping is expected to range from 0.011 - 0.057 kWh/kg (Mani, Tabil and Sokhansanj, 2004; Y. Zhang, 2014). To improve reactor temperature stability and reduce pyrolysis processing energy requirements, the moisture content needs to be reduced to less than 10% (Bridgwater and Peacocke, 2000), and this can be achieved using steam and a trommel. Zhang (2014) assumes a steam requirement of 0.085 kg/kg of pre-treated corn stover and Dang et al. (2014) state an energy requirement of 0.148 kWh/kg of pre-treated corn stover. The pyrolysis non-condensable gases (NCG) are expected to have an HHV of 6 MJ/kg and yields of 10 - 20% are typical (Mullen *et al.*, 2010); thus there would be sufficient gas to combust to meet this demand. For higher pyrolysis oil yields, both the gas and char may need to be used. Using the pyrolysis gases for drying has been assumed in other studies (Peters *et al.*, 2015; Han *et al.*, 2011), and therefore the energy requirement is often neglected.

Table 4.3: Model inputs and output for biomass pre-treatment

Item	Min	Exp	Max	Unit
Inputs				
Electricity for grinding	0.011	0.034	0.057	kWh/kg of pre-treated corn stover
Steam from natural gas boiler	0	0	0.085	kg/kg of pre-treated corn stover
Outputs				
Pre-treated corn stover		0.82		%

4.2.2. Pyrolysis process

The pyrolysis plant is assumed to process 2000 tons per day of prepared corn stover at 500 °C (Wright *et al.*, 2010b; Y. Zhang, 2014). Electricity is typically used as the energy input to a pyrolysis system, with power requirements ranging from 0.14 - 0.487 kWh/kg of bio-oil produced (Dang *et al.*, 2014; Y. Zhang, 2014). A value of 0.417 is suggested in (Y. Zhang, 2014), which has been chosen as the expected value. The yield of bio-oil from the fast pyrolysis of corn stover is typically around 62 - 75wt% (Dang *et al.*, 2014; Y. Zhang, 2014; Han *et al.*, 2011), although yields as high as 80% have been suggested (Bulushev and Ross, 2011). Pyrolysis process inputs and outputs are shown in Table 4.4.

Table 4.4: Bio oil production through pyrolysis – according to GREET database input data (Zhang, 2014; Dang et al., 2014)

Item	Min	Exp	Max	Unit
Inputs				
Electricity used in pyrolysis	0.14	0.417	0.487	kWh/kg kg bio-oil
Outputs				
Bio-oil produced	0.62	0.75	0.80	%

4.2.3. Esterification

Esterification is performed within a temperature range of 70 - 170ºC (Gunawan *et al.*, 2012). The yield of upgraded bio-oil in conventional conditions (100ºC) when using a zeolite catalyst is approximately 62 wt% (Peng *et al.*, 2009). Ideal ethanol to oil ratios of 3:1 (Bulushev and Ross, 2011) and 5:1 (Q. Zhang *et al.*, 2014) have been reported for the esterification process. However, similar yields of upgraded bio-oil (approximately 60%) have been obtained using 2 wt.% sulphuric acid and lower ethanol to oil ratios ranging from 1:1 to 3:1 (Abdul Aziz *et al.*, 2017). Sugar cane, maize and sugar beet are suitable sources for producing bioethanol (Muñoz *et al.*, 2014). For the purposes of this study, bioethanol produced from maize, as given by the Ecoinvent database, has been used. Esterification of the bio-oil in super-critical conditions (250 - 300ºC) has not been considered as it can affect bio-oil composition (Peng *et al.*, 2009). Based on a specific

heat capacity of 2.435 kJ/kg bio-oil (Goteti, 2010), neglecting heat losses, assuming a bio-oil initial temperature of 30 °C and considering the possible operating temperature values (Physics, 2009), the energy requirement is expected to range from 0.027 - 0.095 kWh/kg. Esterification inputs and outputs are presented in Table 4.5.

Table 4.5: Esterification of bio-oil

Item	Min	Exp	Max	Unit
Inputs				
Electricity	0.027	0.061	0.095	kWh/kg of raw bio-oil
Sulphuric acid	-	2	-	wt%
Ethanol	1	2	3	kg/kg of raw bio-oil
Outputs				
Bio-fuel produced	0.55	0.62	0.65	%

4.2.4. Ketonisation

Ketonisation can be performed on the light oxygenates fraction of the pyrolysis oil at around 400 °C (Snell *et al.*, 2013). The quantity of electricity required in the process is calculated (similar to esterification process) to be 0.25 kWh/kg of light oxygenates. Processed bio-oil yields obtained through ketonisation depend on the catalyst, temperature and reaction time, but it is expected to be 54% using a $Ru/TiO_2/C$ catalyst at 5 wt% (Pham *et al.*, 2012). Carbon dioxide formed from the chemical reaction has not been included. Ketonisation inputs and outputs are shown in Table 4.6.

Phase separation of bio-oil into light oxygenate, sugar derived and lignin derived components can be achieved by processing biomass at 300°C to get acetic acid and acetol. This is followed by heating at 400°C to obtain furfurals, and finally processing at 550°C to get phenolics (Pham *et al.*, 2014). The additional energy requirements at the pyrolysis stage to achieve phase separation have not been included. Separation is expected to result in 10% light oxygenate, 30% sugar derived and 60% lignin derived components (Pham *et al.*, 2013; Q. Zhang *et al.*, 2007).

Aldol condensation takes place at 120°C; a 5 wt% $Pd/MgO–ZrO_2$ catalyst is used to process acetone from ketonisation of the light oxygenates and sugar derived oils having

undergone esterification (Barrett *et al.*, 2006). The yield from aldol condensation is expected to be 51.4% (Pham *et al.*, 2014).

Table 4.6: Ketonisation of bio-oil

Item	Min	Exp	Max	Unit
Inputs				
Electricity		0.25		kWh/kg of light oxygenates
Ru/TiO$_2$/C Catalyst		5		wt%
Outputs				
Bio-fuel produced	-	0.46	-	%

4.2.5. Hydroprocessing

Depending on the amount of hydrotreating performed, different degrees of deoxygenation can be achieved. Hydrotreating can also be performed in a single stage or two stage reactor.

4.2.5.1. Singe Stage Hydrotreating

Single-stage hydrotreating is usually conducted for 4 hours using noble metal catalysts (Ru/C and Pd/C) and pressures and temperature of up to 200 bar and 400°C (Wildschut, 2009). Hydrotreating of fast pyrolysis oils at 180 - 250°C and pressures of 130 - 142 bar using ruthenium have been found to reduce oxygen content from around 40 to 18 - 27 wt% (Wildschut, 2009; H. Wang, Male and Wang, 2013). Upgraded bio-oil yields reported for hydrotreating are more variable and range from 30 - 65% (Wright *et al.*, 2010b; Wildschut, 2009; Holmgren *et al.*, 2008b) with the highest yields being obtained when using 5 wt% Ru/C. Hydrotreating pyrolysis oils obtained from corn stover using an Ru/C catalyst can achieve a 25 - 26 wt% oxygenated product and yields between 54 - 67% (Capunitan and Capareda, 2014). Hydrogen consumption for corn stover has been reported to range between 69 and 128 litres per litre of feed; higher values of 205 and 252 litres of hydrogen per litre of feed have been reported for mixed wood and poplar (Dang *et al.*, 2014; D. C. Elliott *et al.*, 2009).

4.2.5.2. Two stage Hydrotreating

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 (S. Jones *et al.*, 2013). The total residence times for two-stage hydrotreating range from 2 to 4 hours (S. Jones *et al.*, 2013; Wildschut, 2009). In the first stage, Ru/C is used, whereas a Pt/C or NiMo catalyst is normally used in the second stage. Catalyst quantities are normally around 3 - 5 wt% (Wildschut *et al.*, 2009; Wildschut, Melián-Cabrera and Heeres, 2010) with lifetimes of 700 to 1752 hours (Snowden-Swan *et al.*, 2016). Therefore, the expected catalyst requirement is 0.1 - 0.3 g/kg of bio-oil, based on a 4 hour residence time. Reports have claimed that two-stage hydrotreating enables a 13% reduction in hydrogen to be achieved (Gandarias and Arias, 2013), whereas other studies have found the hydrogen consumption to remain proportional to the level of deoxygenation (Boscagli *et al.*, 2015). The amount of deoxygenation can be as low as 2 wt% (Han *et al.*, 2011), but 6 - 11 wt% is more likely (H. Wang *et al.*, 2013; Wildschut *et al.*, 2009). Hydrogen consumption is expected to range from 58 g/kg (S. Jones *et al.*, 2013) to 112 g/kg of hydrotreated biofuel (S. B. Jones *et al.*, 2009). Other authors have reported 69 g/kg (Dang *et al.*, 2014). The assumption is made that hydrogen is obtained from conventional steam reforming of natural gas; however, make-up hydrogen could be obtained from the off-gases from the pyrolysis and hydroprocessing stages. The overall yield of deoxygenated bio-oil for two-stage hydrotreating is expected to range from 30 - 44% (S. B. Jones *et al.*, 2009; Zheng, Chang and Fu, 2015).

4.2.5.3. Hydrocracking

Hydrocracking is performed at temperatures between 400 - 450°C and at 100 - 140 bar (Wright *et al.*, 2010b). The catalysts used in the process are 3 - 5 wt% Ni-HZSM-5 zeolites (Weng *et al.*, 2015). Hydrogen consumption can fluctuate between 1.5 wt% to 4.0 wt% (JSC SIE Neftehim, 2015). Output bio-oil yields of 75% are expected (Sayles and Romero, 2011). The amount of deoxygenation after hydrocracking is expected to range from 0.3 - 5 wt% (Wildschut *et al.*, 2009; D. Elliott and Neuenschwander, 1997; D. C. Elliott *et al.*, 2009).

The electricity requirement largely depends on the assumptions made regarding processing temperatures, times and heat losses, pressurisation and pumping. Electricity

requirements for hydrotreating and hydrocracking have been reported to be 0.23 kWh/kg (Dang *et al.*, 2014) and 0.22 kWh/kg of produced biofuel (Y. Zhang, 2014). Electrical energy requirements are very low where the exothermic hydrotreating reactions are considered and values as low as 0.034 kWh/kg and 0.054 kWh/kg have been stated for two-stage hydrotreating and hydrocracking respectively (Iribarren *et al.*, 2012).

Hydrotreating and hydrocracking inputs and outputs are presented in Table 4.7.

Table 4.7: LCA input data for single-stage and two-stage hydrotreating followed by hydrocracking

Item	Min	Exp	Max	Units
Inputs				
Single-stage HT hydrogen consumption	69	74	128	g/kg of HT biofuel
Ru/C Catalyst (first-stage)	0.1	0.2	0.3	g/kg of HT biofuel
Outputs				
Single-stage HT yield of 18-27 wt% deoxygenated biofuel	36	56	67	%
Inputs				
Two-stage HT hydrogen consumption	58	69	112	g/kg of HT biofuel
Pt/C/ Pd/C Catalyst (second-stage)	0.1	0.2	0.3	g/kg of HT biofuel
Outputs				
Two-stage HT yield of 2-11 wt% deoxygenated biofuel	30	38	44	%
Inputs				
HC hydrogen consumption	15	20	40	g/kg of HC biofuel
Zeolite powder for HC	3	5	5	wt%
HC biofuel yield	-	0.75	-	kg/kg of HC biofuel
Outputs				
Total electricity for hydroprocessing	0.088	0.16	0.23	kg/kg of synthetic fuel

4.2.6. Transportation and distribution of synthetic fuel

The synthetic fuel transportation and distribution was assumed to be via a 9.3t payload truck travelling a total distance of 150 km. A minimum and maximum value of 100 km and 200 km are used to account for the possible range in travelled distance (Table 4.8).

Table 4.8: Transportation and distribution of synthetic fuel

Item	Min	Exp	Max	Unit
Inputs				
Diesel	0.1	0.15	0.2	MJ/kg of delivered synthetic fuel
Outputs				
Bio-fuel delivered		1		kg

By analysing Tables 4.1 to 4.8, a wide range was observed in some values, but since all values were taken (or calculated) from previous research in the field, the values were considered reliable. Furthermore, each factor's share of the total CO_2 emissions will be further illustrated and analysed for all min (most optimistic), exp (expected) and max (pessimistic) values.

4.3. Results and analysis

The expected carbon dioxide equivalent emissions associated with the production of synthetic fuel from pyrolysis are shown for each upgrading scenario in Figure 4.1. For comparison, the emissions associated with the production and use of fossil fuel are provided. Error bars indicate the most optimistic (min) and pessimistic (max) CO_{2e} emissions possible for the production (well-to-tank) stage and CO_2 absorbed by feedstock, based on the variation of the inventory data values. For figure clarity, and due to the small and equal variation value for all six scenarios (of 350 gCO_{2e}/kg of synthetic fuel), the error bars for vehicle operation (tank-to-wheel) are not represented.
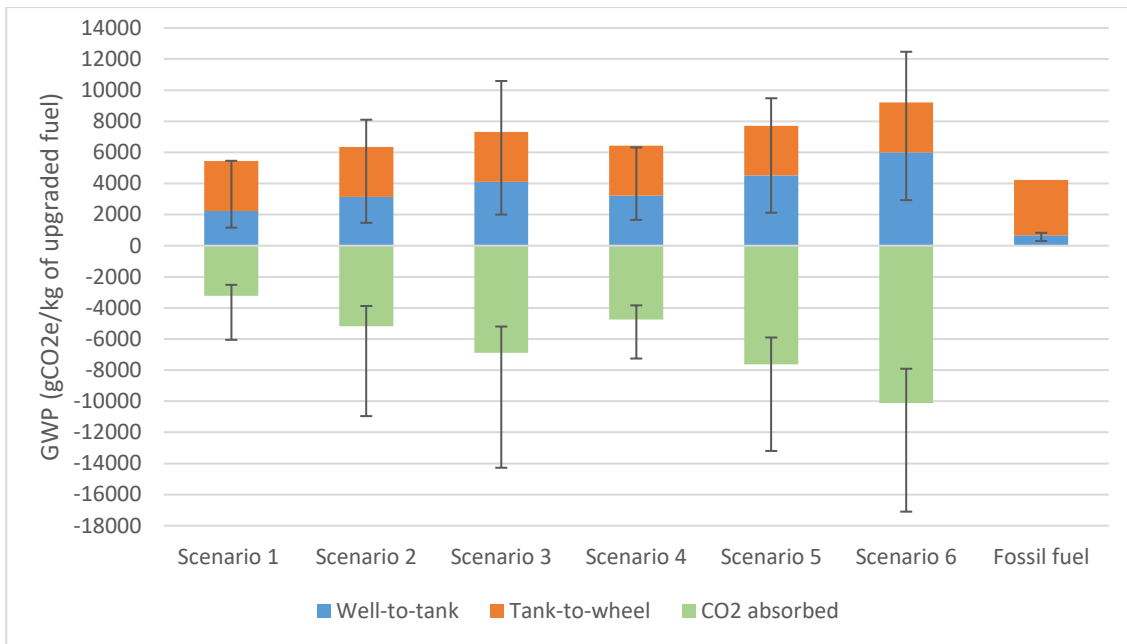
Figure 4.1: The CO_{2e} emissions associated with the production and use of synthetic fuel for six different upgrading scenarios. Error bars are used for the well-to-tank stage and CO_2 absorbed by feedstock to show the minimum and maximum CO_{2e} emissions possible

For synthetic fuel obtained from hydrotreating and hydrocracking pyrolysis oil (scenario 1), the expected climate change potential of 2240 gCO_{2e}/kg of synthetic fuel is around 50% of the CO_{2e} emissions associated with using diesel or petrol fuel. Scenario 1 is the most commonly considered pyrolysis oil upgrading pathway in the literature. The upgraded fuel from scenario one is expected to have a lower heating value of 42 MJ/kg (Peters *et al.*, 2015), which would suggest an impact of 53.6 gCO_{2e}/MJ. This finding is comparable with values reported for similar systems: 39.4 - 55 gCO_{2e}/MJ has been suggested by other researchers for biofuel from corn stover (Y. Zhang, 2014; Dang *et al.*, 2014). Other studies provide values of 38.9 gCO_{2e}/MJ when using hybrid poplar (Snowden-Swan and Male, 2012) and 33.3gCO_{2e}/MJ for southern pine (S. Jones *et al.*, 2013). However, this study reveals the additional CO_{2e} emissions that will arise from further upgrading to improve fuel quality.

The additional upgrading steps in scenarios 2 - 6, make the CO_{2e} emissions comparable or greater than those associated with using fossil fuel. For example, the emissions caused by producing synthetic fuel in scenario 6 are 43% higher than the total CO_{2e} emissions from diesel fuel. The potential to reduce the CO_{2e} emissions is significant

though, as evidenced by the large errors bars. Under more optimistic conditions, the different scenario emissions range from 1160 to 2930 gCO_{2e}/kg, which represent a potential decrease of 47% to 52%.

The CO_{2e} emissions from producing diesel and petrol fuels—referred to as the well-to-tank emissions are around 307 - 659 gCO_{2e}/kg. The vehicle operation, or tank-to-wheel, emissions are approximately 3387 - 3571 gCO_2/kg for diesel and petrol fuels (Eriksson and Ahlgren, 2013). To take into account the CO_2 absorbed during biomass growth and the CO_2 emitted during vehicle operation, several studies have adopted a well-to-wheels approach for analysing synthetic fuels. Peters et al. (2015) use a well-to-wheel approach to determine the emissions from synthetic fuels to be 40 gCO_{2e}/MJ.

The CO_2 emissions released during combustion depend on the carbon content; for synthetic fuel, the CO_2 emissions are expected to be around 2850 - 3200 gCO_2/kg of fuel (Y. Zhang, 2014; Han *et al.*, 2011) and carbon contents of 77 - 89% have been reported for various degrees of hydrodeoxygenation (Mante *et al.*, 2016). In Figure 4.1, the CO_2 absorbed during biomass growth is based on corn stover absorbing 0.83 $kgCO_2$/kg (Zan *et al.*, 2001). Scenario 6 appears more favourable when considering a well-to-wheels analysis, as 12.2 kg of corn stover is required to produce 1 kg of synthetic fuel in scenario 6, whereas, in scenario 1, only 3.8 kg of corn stover is required, which could have significant financial benefits, as less feedstock would have to be collected, transported and processed. Under most optimistic conditions the corn stover to synthetic fuel overall yields increased by 20 - 25%, which might positively influence the production costs.

Whilst vehicle operation emissions can be considered carbon neutral, further details on the downstream use of the various by-products from the different processing stages would be required to give a more accurate representation of the net emissions. When the non-condensable gases are flared or used for heat recovery, up to 17% of the feedstock carbon could be released back into the atmosphere (Mullen *et al.*, 2010), and these emissions are not included in the production emissions. Biochar can act as a long-term carbon sink, enabling as much as 20% of the carbon to be recovered during fast pyrolysis (*ibid*). If the char were combusted to meet the thermal energy requirement in the pyrolysis reactor, credits can be applied to account for the offset fossil fuel requirement; however, the use of electricity is more practical.

Figure 4.2 shows the CO_{2e} emission contributions from the use of electricity, hydrogen, transport, fertilisers, catalysts, ethanol and natural gas. Minimum, expected and maximum values are shown for each scenario. Electricity is the largest contributor with a 50 - 62% expected share of the total emissions. However, for optimistic conditions, the emissions associated with the use of electricity are reduced by around 70%. At 18 - 33%, the second largest CO_{2e} contribution comes from the use of hydrogen. These CO_{2e} emissions could be reduced by around 25 - 29% based on the range of hydrogen consumption values reported in the literature. Fertilisers, transport and catalysts contribute respectively 14 - 17%, 2.2% and 1.2 - 3.0% of the total CO_{2e} emissions. Net CO_{2e} emissions from using ethanol obtained from maize in the US are slightly carbon negative (-20 to -70 gCO_{2e}/kg) and the source of ethanol can influence the results significantly.
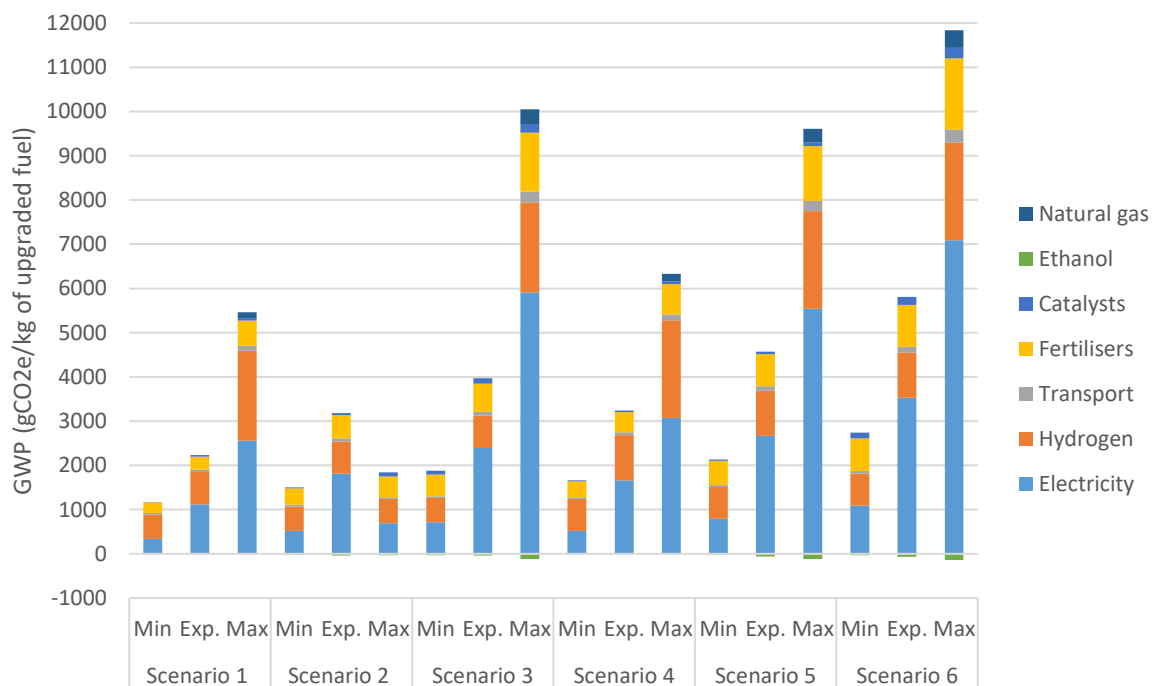
Figure 4.2: Minimum, expected and maximum CO_{2e} emissions associated with the use of electricity, hydrogen, transport, fertilisers, catalysts, ethanol and natural gas during the production of synthetic fuel from pyrolysis oil

The total CO_{2e} emissions from each stage of synthetic fuels production system are shown in Figure 4.3. The expected CO_{2e} emissions prior to bio-oil upgrading are significant with cultivation, pre-treating and pyrolysis accounting for around 54 - 64% of the emissions. In an optimistic scenario, e.g. where energy recovery or alternative

energy sources to electricity can be used, the share of emissions from pyrolysis are reduced by approximately 74%.
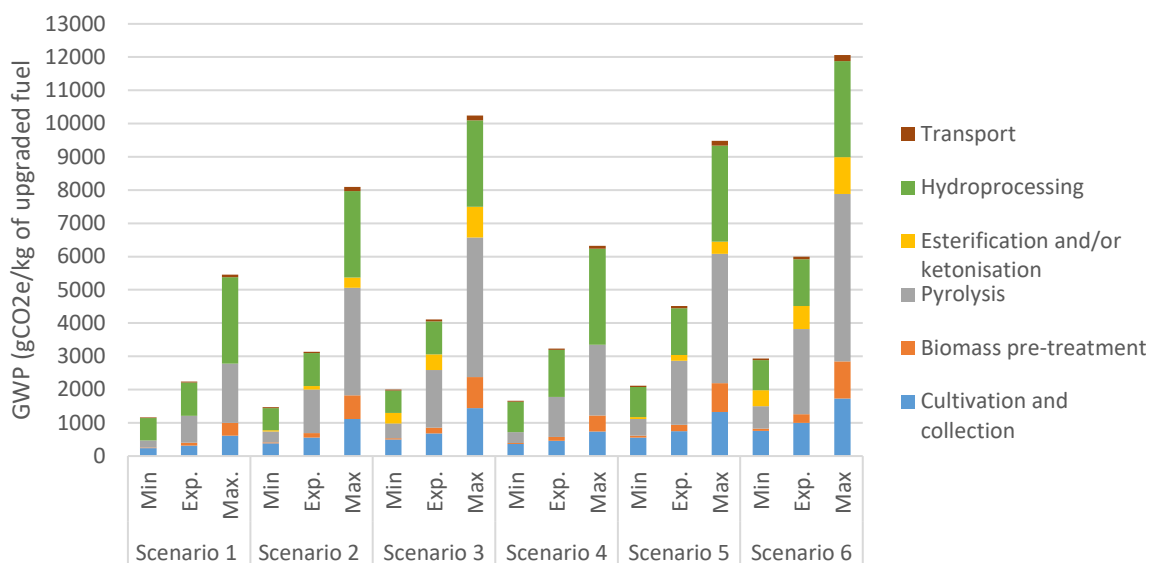
Figure 4.3: Minimum, expected and maximum CO_{2e} emissions associated with each processing stage during the production of synthetic fuel from pyrolysis oil

The high proportion of CO_{2e} emissions associated with hydrogen and electricity highlight the importance of using more sustainable alternatives, which could also reduce operating costs. Moreover, as the pyrolysis and hydroprocessing stages made the most significant contribution to the total CO_{2e} emissions, this identifies that these stages would benefit the most from R&D to achieve gains in environmental and technical performance. The average EU27 electricity grid mix has been used in this study; however, alternative sources such as natural gas, pyrolysis gases and other renewables can be considered.

The pessimistic inventory data provided in this study reveals that the emissions for scenarios 1 - 6 are around 1.5 to 3 times higher than fossil fuel, which is a major concern if facilities and supply chains conduct inefficient practices. This result also highlights the large uncertainty that remains in this field with determining the environmental benefits of using synthetic fuels obtained from the thermochemical conversion of waste feedstocks, and the need for better quality primary data on bio-oil upgrading system performance.

Table 4.9 summarises a series of other impact categories according to the CML 2001 impact assessment method.

Minimum and expected impacts for scenarios 1 - 6 are shown in comparison to low sulphur diesel fuel. Whereas scenario 1 provides environmental advantages over diesel, scenarios 2 - 6 increase several negative environmental impacts. For scenarios 2 - 6, the expected eutrophication and acidification potential ranges respectively from 0.0026 - 0.005 kg PO_4^{3-} eq. and 0.0098 - 0.026 kg SO_2 eq. which are higher than the impacts associated with diesel fuel (0.00167 kg PO_4^{3-} eq and 0.0058 kg SO_2 eq.). This is to be expected due to the higher quantities of fertiliser used in scenarios 2 - 6. Different farming practices can have a significant influence on the fertiliser requirements. The sensitivity of the GWP and eutrophication result for sceanrio1 based on ammonium nitrate usage is further examined in Figure 4.4a. It shows that the eutrophication potential would be reduced to 0.00061 kg PO_4^{3-} eq if the use ammonium nitrate fertiliser was avoided. The element abiotic depletion potential (ADP) is also high in all scenarios as a result of fertiliser usage. Interestingly, the fossil ADP value is also higher than diesel fuel in scenarios 2 - 6, which is a caused by the increased hydrogen consumption in the more advanced upgrading processes. However, the minimum values reveal that saving could be achieved with the exception of scenario 6. The sensitivity of the GWP and fossil ADP values on the hydrogen consumption in scenario 1 is shown in Figure 4.4b. An increase in hydrogen consumption from 50 - 168 g/kg of upgraded fuel doubles the fossil ADP and increases the GWP from around 1.9 to 2.8 kg $CO_{2e.}$ Whilst conventional externally sourced hydrogen from natural gas has been considered in this study, other authors have suggested that internal steam reforming of by-products to produce hydrogen is a more promising option (Dang *et al.*, 2014).

Table 4.9: Environmental impacts conforming to the CML 2001 assessment method for the production of synthetic and diesel fuel:

Impact Categories	Scale	Scenario 1			Scenario 2			Scenario 3			Scenario 4			Scenario 5			Scenario 6			Diesel
		Min	Exp	Max	Min	Exp	Max	Min	Exp	Max	Min	Exp	Max	Min	Exp	Max	Min	Exp	Max	
Acidification Potential (kg SO_2 eq.)	E-03	2.8	4.95	12	4.88	9.78	24	12	18	40	4.04	7.18	14	7.22	14	28	17	27	48	5.82
Eutrophication Potential (kg PO_4^{3-} eq.)	E-03	0.62	1.01	2.15	1.26	2.61	5.94	1.84	3.34	7.74	0.92	1.47	2.53	1.9	3.57	7.08	2.78	4.91	9.25	1,67
Ozone layer depletion potential (kg R11 eq.) [a]	E-07	0.19	0.27	0.57	0.42	0.76	1.69	0.60	0.96	2.23	0.29	0.4	0.68	0.64	1.03	2.03	0.92	1.41	2.67	6.9
Abiotic depletion element (kg Sb eq.)	E-07	16.8	26.5	53.88	28.7	50	111	47.8	75.1	160	25.2	39	63.9	43.3	71.5	132	72.5	110	191	4.74
Abiotic depletion fossil (MJ)	E+01	3.26	5.16	13.8	3.73	6.52	17.7	4.14	7.41	20	4.44	7.31	15.4	5.15	9.25	2.02	5.77	10.7	22.8	5.36
Freshwater aquatic ecotoxicity potential (kg DCB eq.) [b]	E-02	6.2	9.5	18	12.4	23.9	51.3	21.5	34.5	74.1	9.3	14	21.5	18.9	32.8	61.4	32.7	50.9	88.8	8.6
Human toxicity Potential (kg DCB eq.)	E-01	1.81	2.75	5.77	3.15	5.51	12.5	4.37	7.1	16.2	2.7	4.03	6.83	4.75	7.79	15	6.61	10.4	19.3	2.71
Marine aquatic ecotoxicity potential (kg DCB eq.)	E+02	2.27	3.96	8.19	4.11	8.46	18.6	6.09	10.1	24.6	3.43	5.82	9.76	6.23	11.5	22.2	9.24	16	29.5	2.79
Photochemical oxidant creation potential (kg C_2H_4 eq.)	E-04	2.01	3.45	9.19	3.01	5.87	15.2	7.51	11.6	26	2.97	5.06	10.5	4.46	8.34	17.7	10.1	17.1	28	5.72
Terrestrial ecotoxicity potential (kg DCB eq.)	E-03	2.55	3.92	8	5.16	9.98	22	7.02	12	28	3.87	5.75	9.57	7.84	14	26	11	18	33	3.43

[a] Trichlorofluoromethane equivalent (R11 eq.)

[b] Dichlorobenzene equivalent (DCB eq.)
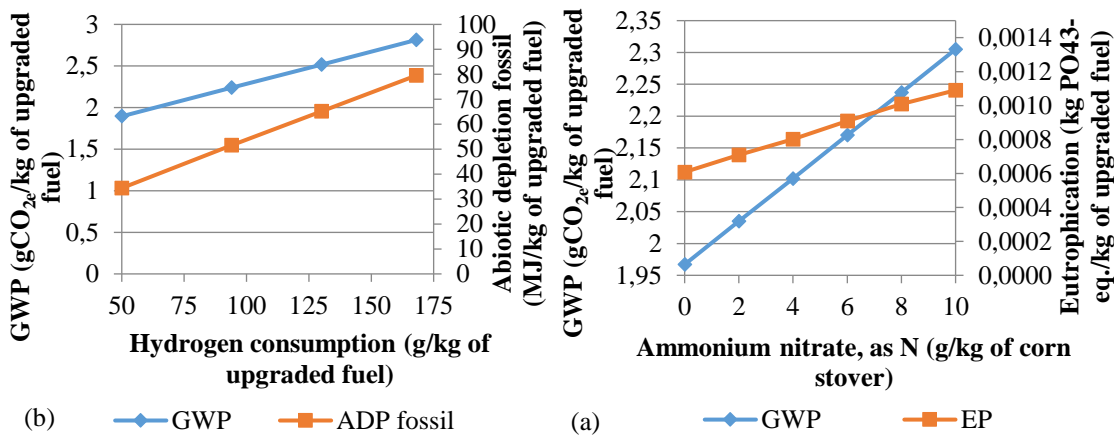
Figure 4.4: a-b: Sensitivity of the environmental impacts arising from scenario 1 based on ammonium nitrate (a) and hydrogen (b) usage

Future LCA studies on synthetic fuels must consider the wide range of environmental impacts that occur during the production of synthetic fuels, as many negative environmental impacts increase in comparison to the diesel and petrol production processes. In further work, the materials used in system construction could also be taken into account. Different allocation methods for stover and pyrolysis by-products need to be investigated, for adding fuel production into the existing corn production system to see if environmental benefits can be gained. For example, economic and energy-based allocation methods have been compared for corn and stover production (Murphy and Kendall, 2013). A displacement approach could also be considered as corn stover would likely be used elsewhere (e.g. as cattle feed). As more and more companies seek to commercialise the production of synthetic fuel via pyrolysis, great care must be taken to ensure that environmental gains over conventional fossil fuels are being achieved and a trade-off between environmental impact, cost and product quality has to be made.

4.4. Hydrogen source sensitivity study

For sensitivity analysis, in scenario 1, internally hydrogen was produced through steam reforming of pyrolysis bio-oil aqueous phase (Marker *et al.*, 2005; C. Yan *et al.*, 2010).

The environmental impacts of Scenario 1 with external hydrogen, internal hydrogen produced by steam reforming 38% of the bio-oil and internal hydrogen produced by steam reforming of the natural gas were obtained by using GaBi software and are presented in Table 4.10.

Table 4.10: Comparison for Scenario 1's environmental impacts using different sources of hydrogen.

H$_2$ source / Impact	Scale	Scenario 1 Ext H$_2$ (merchant - Op1)	Scenario 1 Int H$_2$ (aq. Phase - Op2)	Scenario 1 Int H$_2$ (natural gas - Op.3)
Global Warming Potential (kg CO$_2$ eq.)	E-03	2240	3010	2530
Acidification Potential (kg SO$_2$ eq.)	E-03	4.95	6.43	13
Eutrophication Potential (kg PO$_4^{3-}$ eq.)	E-03	1.01	1.57	1.63
Ozone layer depletion potential (kg R11 eq.) [a]	E-07	0.27	0.42	2.6
Abiotic depletion element (kg Sb eq.)	E-06	2.65	4.01	3.06
Abiotic depletion fossil (MJ)	E+01	5.16	3.15	6.39
Freshwater aquatic ecotoxicity potential (kg DCB eq.) [b]	E-02	9.5	16.9	27.7
Human toxicity Potential (kg DCB eq.)	E-01	2.75	4.1	6.09
Marine aquatic ecotoxicity potential (kg DCB eq.)	E+02	3.96	6.75	10.3
Photochemical oxidant creation potential (kg C$_2$H$_4$ eq.)	E-04	3.45	2.85	8.00
Terrestrial ecotoxicity potential (kg DCB eq.)	E-03	3.92	6.63	6.04
Capital cost ($)	-	0.11	0.23	0.23
Operational cost ($)	-	0.97	0.76	0.74
Min selling price ($)	-	1.42	1.32	1.29

It was found that producing hydrogen inside the plant from the aqueous phase of the bio-oil will result in more carbon emissions but will decrease the fossil fuel depletion by almost 40%. It was found that producing hydrogen inside the plant from natural gas will not improve the environmental impact compared with acquiring the hydrogen from an

external source. Moreover, the fossil fuel depletion is higher than fossil diesel. Therefore, it was not included further in this study.

By using the internal hydrogen production source (Op2) it was found an overall increase of 25 - 33% in the CO_2 emissions of the six scenarios, compared to the external source (Op1) – due to a 62% increase in biomass usage to get the same yield of upgraded fuel. The energy environmental impact showed the highest growth in the CO_2 emissions, increasing by 53% due to its use in hydrogen production; the fertilisers impact increased with 32 - 29% and transport impact with 29 - 38%.

4.5. Conclusions

This section identifies that favourable CO_{2e} emission reductions can be achieved by using synthetic fuel from pyrolysis in comparison to conventional diesel fuel. However, if inefficient practices are followed, a low quality synthetic fuel that nearly triples CO_{2e} emissions in comparison to fossil fuel will be produced. High quality fuels obtained via esterification, two-stage hydrotreating and hydrocracking, or esterification, ketonisation, adol condensation, two-stage hydrotreating and hydrocracking, are expected to increase a range of other environmental impact indicators. Esterification and single-stage hydrotreating (scenario 2) or two-stage hydrotreating (scenario 4) can provide a reasonable trade-off between product quality and achievable environmental gains.

It was found that electricity was the main contributor to the CO_2 emissions with 50 - 62% for the external hydrogen production and increased by 53% for the internal hydrogen production. Therefore, future work might consider a pyrolysis plant powered by energy produced by renewable energy sources (e.g. solar or wind).

The by-products were not taken into account in this or any other previous studies in the field. Whilst the assumption is made that the reliability of the results is not affected by the exclusion of by-production considerations, further studies are needed to determine how the environmental impacts could be improved by the exploitation of by-production.

<div align="center">

Chapter 5

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5. Economic Analysis of Bio-Oil with Different Upgrading Pathways

5.1. Introduction

The objective of this chapter is to evaluate the economic feasibility of the pyrolysis process and six different upgrading paths. In this chapter, two different methods of acquiring hydrogen are considered: from merchant and obtained inside the plant from steam reforming of the bio-oil aqueous phase. This study follows a similar methodology to Jones et al. (2009), Wright et al. (2010b), Jones et al. (2013) and Zhang et al. (2013) to calculate the fuel price from each of the scenarios proposed (see Section 2.5). The minimum selling price of one kilogram of synthetic fuel is calculated based on the capital, operational and other costs and taxes. In contrast to the previous studies, the share of each process is shown for the operational cost; and the share of each factor (utility, material, tax, etc.) is shown for the minimum selling cost. Furthermore, a sensitivity analysis examines which factors have the highest influence on the final cost.

5.1.1. Literature review

Previous techno-economic analyses has attempted to quantify the economic sustainability for different upgrading pathways. Wright et al. (2010b; 2010a) conducted a techno-economic study on biomass fast pyrolysis to transportation fuels to analyse the cost of producing naphtha and diesel range fuels, for a plant with a capacity of 2000 metric tons per day. They considered two scenarios based on different hydrogen sources. The first scenario assumed 38% of the total bio-oil being used to produce hydrogen internally, and the second scenario assumed that hydrogen was purchased from an external source. Wright et al. obtained a cost of $0.82 per litre by using internal hydrogen, because of the reduction in the amount of bio-oil converted into biofuel; and a cost of $0.56 per litre by using external hydrogen. A sensitivity analysis showed a variation of cost with the upgrading yield in the first scenario, resulting in a fuel cost of

up to $1.03 per litre. By using regression data from the RAND Corporation, their biofuel cost increased to $1.73 and $0.90 per litre in the first and second scenarios, respectively.

Zhang (2013; 2014) conducted a techno-economic study on two bio-oil upgrading pathways: one consisted of two-stage hydrotreating followed by fluid catalytic cracking and the second one consisted of single-stage hydrotreating followed by hydrocracking, for a plant with a capacity of 2000 metric tons per day. They imply two different sources of acquiring hydrogen: merchant hydrogen or hydrogen from natural gas reforming. Following a sensitivity analysis, they concluded that product yield, fixed capital investment and biomass cost have the greatest impacts on the facility's internal rate of return. However, the study does not provide detail on the chemical and fuel costs that would result from each scenario.

Marker et al. (2005) conducted a study for UOP (Universal Oil Products) to upgrade pyrolytic lignin. Assuming that the price of the pyrolysis oil is available at $0.11 per litre, they obtained gasoline and diesel at a price of approximately $0.30/litre. Further, Holmgren (2008b; 2008a) estimates the cost of naphtha and diesel costs obtained from corn stover to $0.48 per litre. Jones et al. (2009) conducted a study to analyse the production of gasoline and diesel from fast pyrolysis of woody biomass, with subsequent hydrotreating and hydrocracking, for a plant with a capacity of 2000 dry metric tons per day. It was found that the cost of naphtha and diesel fuels for a stand-alone biorefinery would be $0.54 per litre.

Jones and Male (2012) projected that the minimum fuel selling price can be reduced to $0.61 per litre; but later – in a further study – Jones et al. (2013) found the minimum fuel selling price to be around $0.90 per litre ($0.89 per litre of gasoline and $0.99 per litre of diesel). Dutta et al. (2015) conducted a process design and analysis of the economics study for the conversion of lignocellulosic biomass to hydrocarbon fuels through thermochemical pathways. They assumed that the fluidised bed fast pyrolysis equipment can be ex situ (fast pyrolysis reactor) or in situ (catalytic fast pyrolysis reactor) and gasoline price can vary between $0.87 per litre (ex situ) and $0.90 per litre (in situ); diesel price can vary between $0.98 per litre (ex situ) and $1.03 per litre (in situ).

5.2. Financial data

The financial data contains the capital and operational costs of each scenario and the plant assumptions. It was gathered from similar studies and from calculations based on cost estimations.

5.2.1. Capital Cost

Zhang (2013) considered the installed equipment cost for bio-oil production, internal hydrogen production, hydrotreating and hydrocracking to be $190 million, from which $69 million represented the cost for the hydrotreating/hydrocraking facility. If external natural gas was used, the cost of the entire process reduced by $23 million due to the equipment cost for the natural gas reforming process. The fixed capital investment was obtained by summing the installed cost, the indirect cost and a contingency cost, resulting in a total cost of $296 million when internal hydrogen is produced and $260 million when external hydrogen is used. Wright et al. (2010b) considered the capital cost for the same capacity and equipment to be $287 million when hydrogen was produced internally and $200 million when the hydrogen was acquired eternally. Jones et al. (2009) analysed a plant designed for the same capacity, and the equipment was found to be $303 million when the hydrogen was produced internally. The installed equipment cost was $92 million for a fast pyrolysis unit, $81 million for a hydrotreating unit, $29 million for a hydrocracking unit, $86 million for the hydrogen generation and $14 million for other utilities. For the same plant capacity, Jones et al. (2013) found that the installed equipment cost of a pyrolysis process and quenching unit would be $162 million; for the hydrotreatment process, $115 million - $88 million would be for the cost of the hydrotreatment reactors; the hydrocracking cost would be $19 million; the hydrogen generation would cost $69 million and other costs of $22 million are considered. The total installed equipment cost was therefore estimated to be $387 million.

An integrated plant may reduce costs by $115 million (S. B. Jones *et al.*, 2009). It was assumed that one-stage hydrotreatment makes up 50% of the total cost, resulting in between $40.5 million (S. B. Jones *et al.*, 2009) and $44 million (S. Jones *et al.*, 2013) for external hydrogen purchase and $71 million (S. Jones *et al.*, 2013) for internal hydrogen purchase.

The esterification and ketonisation reactor prices were calculated using online price estimates (Alibaba.com, 2018). The esterification reactor has to process up to 1400 kg bio–oil per day. Considering the ethanol to bio-oil ratios, the ethanol and bio-oil densities and the esterification reaction time (Abdul Aziz *et al.*, 2017; Gunawan *et al.*, 2012), it was found that esterification must be is performed in a Quartz Batch Reactor (Abdul Aziz *et al.*, 2017; Gunawan *et al.*, 2012) with a capacity of 600,000l. It was assumed that ketonisation and aldol condensation can be performed in the same reactor (Gürbüz, Kunkes and Dumesic, 2010). Since only 10% of the bio-oil is ketonised, and considering the bio-oil density and ketonisation reaction time, results in the need for a Stainless Steel Batch Reactor (Pham *et al.*, 2014) with a capacity of 20,000l.

The FCI costs of esterification and ketonisation have been calculated based on the FCI capital cost estimation for a nth plant (Y. Zhang *et al.*, 2013) (see Table 5.1); and TPEC (total price equipment cost) were obtained from online estimations (Alibaba.com, 2018).

Table 5.1: Capital cost estimation for a nth plant (Zhang, 2014) for esterification and ketonisation facilities.

Costs	Formula
TIC (total installed cost)	3.02 x TPEC
IC (indirect costs)	0.89 x TPEC
TDIC (total direct and indirect costs)	TIC + IC
Contingency	20% of TDIC
FCI	TDIC + Contingency

A capital cost between $34 million and $68 million was obtained for the esterification process and a cost of approximately $2 million was obtained for the ketonisation process.

The capital costs considered for this study are presented in Table 5.2.

Table 5.2: The capital costs of fast pyrolysis and HDO, esterification & ketonisation

Capital Cost	Unit	Min Cost	Exp Cost	Max Cost	References:
Fast pyrolysis & HDO (1 stage HT & Ext H_2)	Million $	156	173 / 219.5	274	(S. Jones et al., 2013)
Fast pyrolysis & HDO (2 stage HT & Ext H_2)	Million $	200	217 / 260	318	(Y. Zhang et al., 2013) (Wright et al., 2010b)
Fast pyrolysis & HDO (1 stage HT & Int H_2)	Million $	243	255.5 / 259	306	(S. B. Jones et al., 2009)
Fast pyrolysis & HDO (2 stage HT & Int H_2)	Million $	287	296 / 303	387	
Esterification	Million $	34	51	68	Calc.
Ketonisation	Million $	-	2	-	Calc.

5.2.2. Operational Cost

The price of purchase a kilogram of corn stover feedstock was estimated to be $0.072 /kg. Corn stover feedstock prices of $0.08 /kg (S. Jones et al., 2013; T. R. Brown et al., 2012; Y. Zhang et al., 2013), $0.072 /kg (Edwards, 2007), $0.06 /kg (Han et al., 2011; Qureshi, Hodge and Vertes, 2014) and $0.035 - 0.046 /kg (McAloon et al., 2000) have been reported. A range of $0.05 - 0.1 /kg, with an expected value of $0.075 was assumed by Zhang et al. (2013), and a range of $0.055 - 0.011 /kg, with an expected value of $0.083 was assumed by Wright et al. (Wright et al., 2010b). However, for this study, a range of $0.044 - 0.1 /kg with an expected value of $0.072 was considered, due to literature review findings.

The electricity cost was found to be around $0.054 - 0.061 per kWh (Wright et al., 2010b; Y. Zhang et al., 2013), but Shemfe et al. (Shemfe, Gu and Ranganathan, 2015) assumed an electricity price of $0.18 (£0.15) per kWh. Expected industrial electricity prices of $0.0682 per kWh (EIA, 2018) and $0.103 (€0.088) per kWh (Grubb and Drummond, 2018) were recently reported in the US and EU, respectively. For this study, the electricity price was expected to be $0.065 per kWh, with a minimum value of $0.054 per kWh and maximum value of $0.103 per kWh.

The diesel price was assumed to be between $1 /kg ($0.85 /l - USA) and $2/kg ($1.70 /l - UK) (GlobalPetrolPrices, 2018), with a mean value of $1.5 /kg. The price of hydrogen has been reported to be $1.5 /kg (Wright *et al.*, 2010b), $2 /kg (T. R. Brown *et al.*, 2012) and $3.33 /kg (Y. Zhang *et al.*, 2013); the expected cost in this study is taken as $2.4 /kg. However, hydrogen prices could vary from $0.98 to $1.96 /kg (Wright *et al.*, 2010b), $1.6 to $2.5 /kg (T. R. Brown *et al.*, 2012) and $2.33 to $4.33 /kg (Y. Zhang *et al.*, 2013), and thus for this study a minimum value of $0.98 /kg and a maximum of $4.33 /kg were considered.

The Ru/C catalyst was found to be $5.6 /kg and Pt/C $56.29 /kg, and the zeolite powder was $1.6 /kg (T. R. Brown *et al.*, 2012; Y. Zhang *et al.*, 2013).

Ethanol price is dependent on the feedstock costs. Therefore, for maize ethanol, prices between $0.24 and $0.36 per kg were found (Kwiatkowski *et al.*, 2006). Based on the maize-ethanol prices and the global price of corn, it was assumed that the values above are corresponding to minimum and mean values; and the maximum possible cost of maize ethanol was assumed to be $0.48 /kg. For cellulosic ethanol from corn stover, costs were found to be approximately $0.13 /kg (McAloon *et al.*, 2000; Qureshi *et al.*, 2014). As corn stover price is approximately 40% of the cost of cellulosic ethanol (Saini, Saini and Tewari, 2015), mean and maximum values of $0.18 and $0.25 per kg were assumed.

Sulphuric acid was used in the esterification process - the cost can vary from $30 to $250 per kg with an expected value of $60 /kg (Boyd *et al.*, 2014).

The process water used was found to be between $0.032 per MT (Y. Zhang *et al.*, 2013) and $0.07 per MT (S. Jones *et al.*, 2013), resulting in an expected value of $0.051 per MT. Approximately 15% of the total process water was assumed to be used in the bio-oil production by the cooling tower, with 85% being used for the hydrogen production by the steam reformer (S. Jones *et al.*, 2013).

The ash disposal was found to range from approximately $0.02 per ton ($19.84/MT) (Y. Zhang *et al.*, 2013) at the low end to $0.13 (£0.11) per ton (Shemfe *et al.*, 2015) and $0.18 per ton (S. Jones *et al.*, 2013) at the high end.

The char can be burned and reused in the system (S. Jones *et al.*, 2013) or can be sold; the char credit was assumed to be between \$0.18 per ton (Y. Zhang *et al.*, 2013); and from \$0.01 to \$0.03 per ton (Wright *et al.*, 2010b).

The inventory data of operational costs is summarised in Table 5.3.

Table 5.3: Material and operating parameters employed in estimation

Commodity	Unit	Min Op Cost	Exp Op Cost	Max Op Cost	References:
Feedstock (incl. fert. and diesel)	\$ per kilogram	0.044 0.05	0.72 0.075 0.083	0.10 0.11	(Y. Zhang *et al.*, 2013), (Wright *et al.*, 2010b), (Edwards, 2007), (McAloon *et al.*, 2000)
Electricity	\$ per kwh	0.054	0.061 0.0636 0.0682 0.0689	0.103 0.18	(EIA, 2018), (Grubb and Drummond, 2018), (Shemfe *et al.*, 2015), (S. Jones *et al.*, 2013), (Y. Zhang *et al.*, 2013), (Wright *et al.*, 2010b), (S. B. Jones *et al.*, 2009)
Hydrogen	\$ per kilogram	0.98	1.5 3.33	4.33	(Y. Zhang *et al.*, 2013), (Wright *et al.*, 2010b)
Ru	\$ per kilogram	-	3.89	5.60	(BASF, 2017), (Y. Zhang *et al.*, 2013), (T. R. Brown *et al.*, 2012)
Pt	\$ per kilogram	-	29.24	56.29	(BASF, 2017), (Y. Zhang *et al.*, 2013), (T. R. Brown *et al.*, 2012)
Pd	\$ per kilogram	-	30.67	-	(BASF, 2017)
Zeolite	\$ per kilogram	-	1.60	-	(Y. Zhang *et al.*, 2013), (T. R. Brown *et al.*, 2012)
Ethanol	\$ per kilogram	0.24 0.13	0.36 0.18	0.48 0.25	(Saini *et al.*, 2015), (Qureshi *et al.*, 2014), (Kwiatkowski *et al.*, 2006), (McAloon *et al.*, 2000)
Sulphuric acid	\$ per kilogram	30	50 70	250	(Boyd *et al.*, 2014)
Diesel	\$ per kilogram	1	1.5	2	(GlobalPetrolPrices, 2018)
Process water	\$ per MT	0.032	-	0.07	(Y. Zhang *et al.*, 2013), (S. Jones *et al.*, 2013)
Solid/ash disposal	\$ per ton	0.02	0.13	0.18	(Shemfe *et al.*, 2015), (S. Jones *et al.*, 2013), (Y. Zhang *et al.*, 2013)
Char	\$ per ton	0.01	0.018	0.03	(Y. Zhang *et al.*, 2013), (Wright *et al.*, 2010b)

The operational cost values indicated a wide range with some outliers values, but since all values were collected from previous research in the field, it was assumed that the

values were reliable. Furthermore, each factor's share of the total cost will be further identified and the main influencing values will be analysed in a sensitivity study.

5.2.3. Plant assumptions

The plant life, plant financing debt/equity, term for debt financing, interest rate for debt financing, on-steam factor, income tax rate (ITR), working capital cost (WCC), internal rate of return (IRR) were assumed accordingly with Table 5.4.

Table 5.4: Plant assumptions

Assumption Description	Unit	Assumed min value	Assumed exp value	Assumed max value	References:
Plant life	years	-	20	30	(Shemfe *et al.*, 2015), (S. Jones *et al.*, 2013), (Y. Zhang *et al.*, 2013), (T. R. Brown *et al.*, 2012), (Wright *et al.*, 2010b), (S. B. Jones *et al.*, 2009)
Plant financing debt/equity	% of total investment	40	50	60	(S. Jones *et al.*, 2013)
Term for debt financing	years	5	10	20	(S. Jones *et al.*, 2013)
Interest rate for debt financing	%	-	8	-	(S. Jones *et al.*, 2013)
On-stream factor	days	328.5 329 days	350 days	365 days (max.)	(S. Jones *et al.*, 2013), (Wright *et al.*, 2010a), (Wright *et al.*, 2010b)
Income tax rate	%	31	35 - 39	45 49	(Citizens Advice, 2017), (S. Jones *et al.*, 2013), (Y. Zhang *et al.*, 2013)
Working capital cost	%	12 5	15	22.5	(S. Jones *et al.*, 2013), (Y. Zhang *et al.*, 2013)
Internal rate of return	%	5	10 9.8	15	(Shemfe *et al.*, 2015), (S. Jones *et al.*, 2013), (Wright *et al.*, 2010b), (Y. Zhang *et al.*, 2013)

5.3. Results and analysis

To calculate the total costs, an interest rate for debt financing of 8% (S. Jones *et al.*, 2013) was assumed for the capital cost and was added to the capital and operational costs. Furthermore, to calculate the minimum selling price of each scenario, on-stream factor, working capital cost, income tax rate and internal rate of return were added to the total costs.

The impact of the capital cost on each scenario was calculated assuming that the time to payback the entire investment would be 10 years (S. Jones *et al.*, 2013) – as it was found to be the preferred timeframe in previous studies and was considered to be the best option for this study, taking into account that the plant life was assumed to be 20 years (T. R. Brown *et al.*, 2012; S. B. Jones *et al.*, 2009). Because shutdowns for repairs and maintenance the plant was assumed to operate 350 days/year (Wright *et al.*, 2010a). The minimum, expected (most likely) and maximum capital cost of each scenario are presented in Figure 5.1. If the plant operates 329 days/year (Wright *et al.*, 2010b), the costs increase between $0.10 - 0.30 per ton of synthetic fuel.
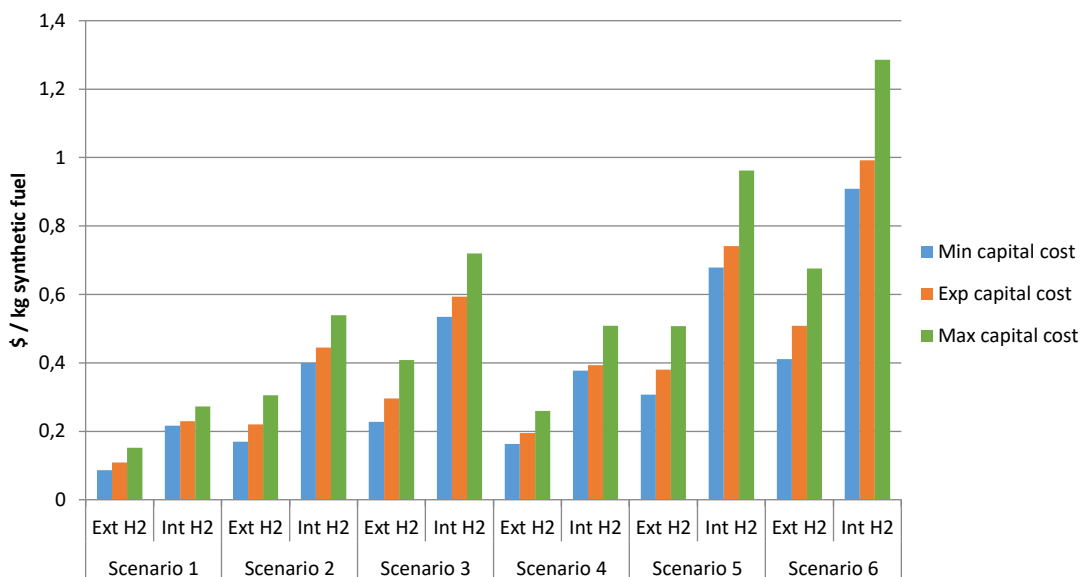
Figure 5.1: Minimum, Expected and Maximum capital costs of the six scenarios

In the most likely case (expected), if the hydrogen is produced in the plant the capital costs increase by $12 - 48 per ton of synthetic fuel produced when the plants operates

for 350 days/year; and with $13 - 53 per ton of synthetic fuel produced when the plants operates for 329 days/year.

The expected, minimum (optimistic) and maximum (pessimistic) operational costs involved in each scenario are presented in Figure 5.2; they were calculated based on the expected (exp), minimum (min) and maximum (max) input data (see sections 4.2 and 5.2.2), considering the expected output data (see sections 4.2).
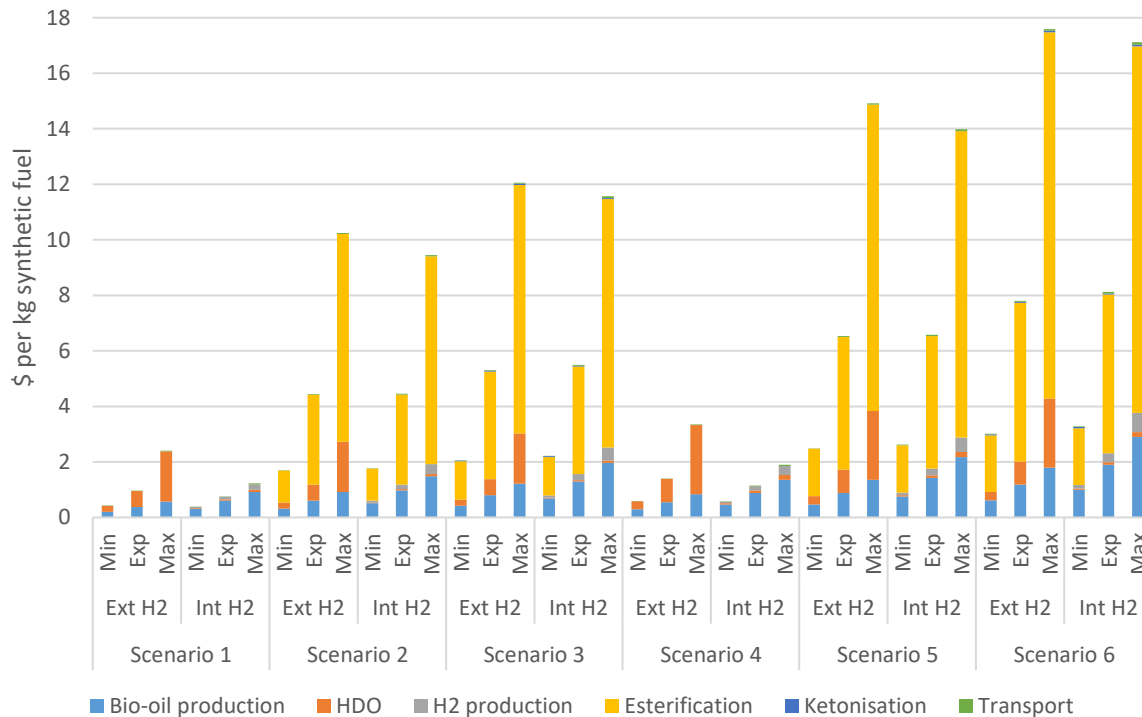
Figure 5.2: Minimum, Expected and Maximum operational costs associated with each process, and the costs in relation to the source of hydrogen, for the six upgrading scenarios.

In the most expected cases, production costs were lower for Scenarios 1 & 4 when internally produced hydrogen was used; but in Scenarios 2, 3, 5 & 6, the costs were improved when externally produced hydrogen was used. In Scenarios 1 & 4, the operational cost decreased by 18 - 22% when the hydrogen was produced internally through steam reforming of the bio-oil aqueous phase; in Scenarios 2 & 5 the operational cost was similar for both sources of hydrogen. For Scenarios 3 & 6, purchasing hydrogen seems to be a more suitable option as it would reduce operational cost by approximately 4%.

The main contributors to the total operational cost were found to be the bio-oil production, HDO and esterification. Bio-oil production and HDO (including H_2 purchase or production) were the main contributors of Scenarios 1 & 4 with shares of up to 39% and 60% respectively when the hydrogen was purchased externally; and up to 80% and 21% respectively when the hydrogen was produced internally. The main contributor to the total operational cost of Scenarios 2, 3 5 & 6 was found to be the esterification process, with 70 - 73%, the second largest contributor was bio-oil production with shares of 13 - 23% and the HDO (including H_2 purchase or production) with a contribution of 1 - 13%. For scenarios 3 and 6, the ketonisation process contributed less than 1% of the total operational cost.

As shown in the previous chapter (Section 4.3), from 1 kg of corn stover, Scenario 1 produced 0.26 kg of synthetic fuel, whereas, because of the additional processes associated with scenario 6, this process produced only 0.08 kg of synthetic fuel. Under the most optimistic conditions synthetic fuel yields of the six scenarios improved by 20 - 25%. Figure 5.3 illustrates the operational costs obtained by using the expected yields of synthetic fuel in comparison to the most optimistic and pessimistic yields of synthetic fuel (see Tables 4.1 - 4.8 output data). The expected, most optimistic (min) and pessimistic (max) case scenarios were considered (see Figure 5.2).

Figure 5.3 (a) Operational costs variation for Min and Max output yield – for expected costs
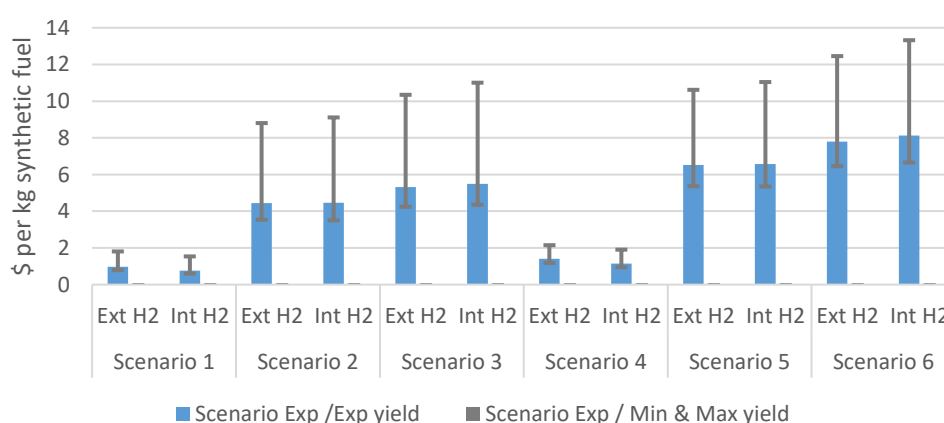
Figure 5.3 (b) Optimistic Operational cost variations for Min and Max output yield
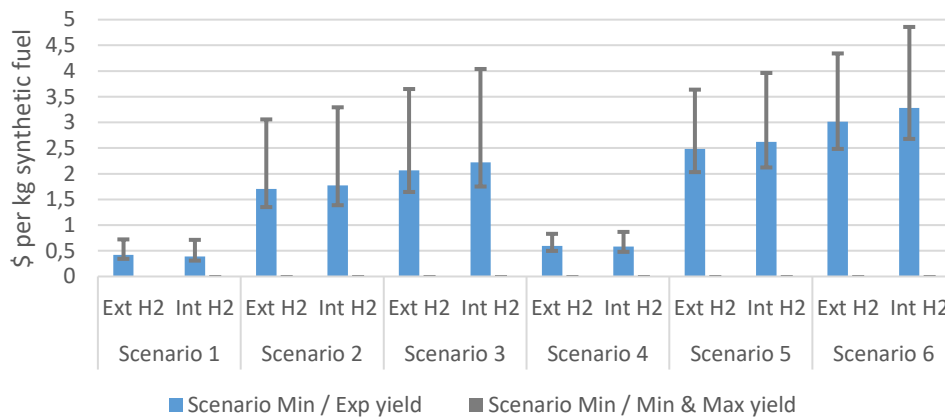
Figure 5.3 (c) Pessimistic operational cost variations for Min and Max output yield
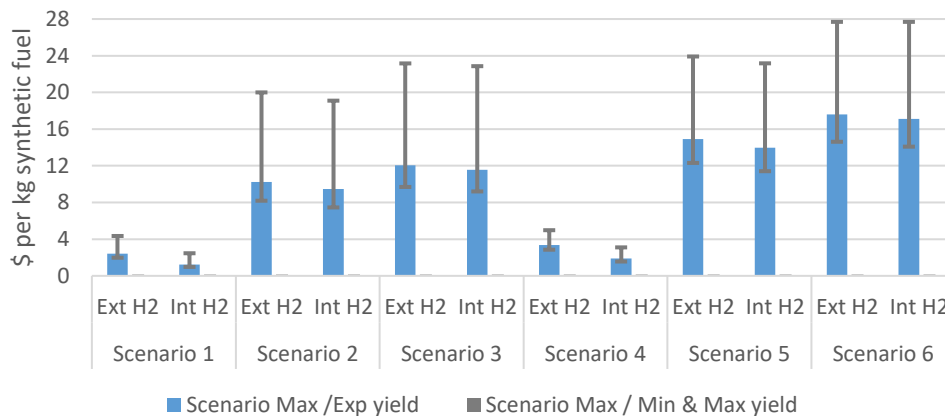
Figure 5.3: Error bars show the operational cost variation for the most optimistic and pessimistic yields compared to the expected yield, for most expected (a), most optimistic (b) and pessimistic (c) case scenarios, for both external and internal hydrogen production sources.

Figure 5.3 highlights that by optimising the output yield of the whole process, the operational costs of the six scenarios decreased by between 16 - 20% when the hydrogen was produced externally; and when the hydrogen was produced internally the operational costs improved by 12 - 24%. Further research may be therefore needed to optimise bio-oil production, esterification and HDO to improve the cost of synthetic fuels.

The expected total cost of 1 kg of synthetic fuel was calculated by adding the capital and operational costs together and multiply the resulted cost with the working capital cost of 15% and the internal rate of return of 10%. An income tax rate of 39% was

added to the internal rate of return. The resulting cost was assumed to be the minimum cost of selling of the synthetic fuel and it is presented in Figure 5.4. The error bars represent the minimum and maximum cost. The minimum and maximum selling cost assumed working capital costs of 12 and 22.5%, internal rates of return of 5 and 15% and income tax rates of 31 and 49%.
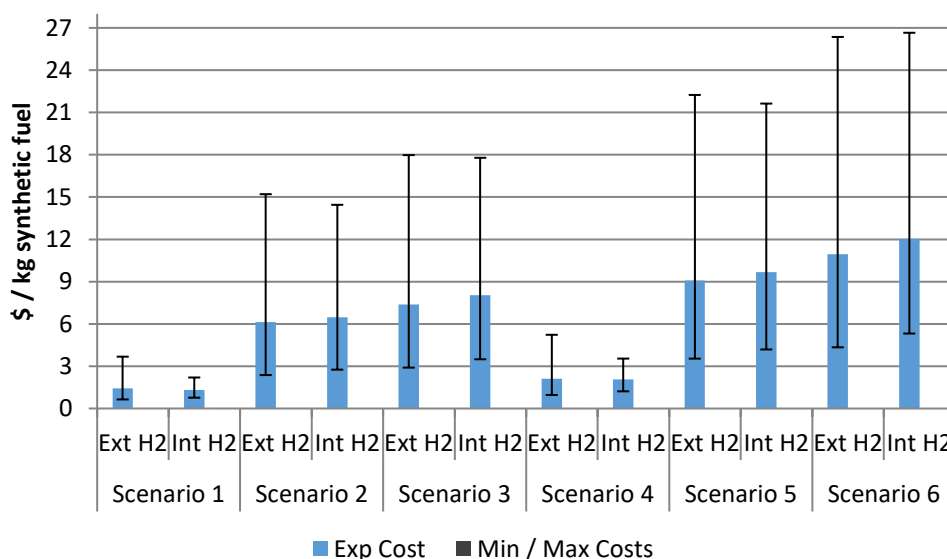
Figure 5.4: Expected selling costs of the six scenarios and bars representing minimum and maximum possible selling costs

From Figure 5.4, it can be noticed that the minimum selling price in Scenarios 1 and 4 was between $1.42 - 2.12 per kg of synthetic fuel produced in the expected case, between $0.64 - 0.96 per kg of synthetic fuel produced in the most optimistic case, and between $3.68 - 5.23 per kg of synthetic fuel produced in the pessimistic case. When the hydrogen was produced internally the price decreased by 2 - 8% compared with external hydrogen production in the expected case, but increased by 19 - 27% in the optimistic case. In Scenarios 2, 3, 5 & 6 the prices varied from $6.13 to $10.94 per kg of synthetic fuel produced in the expected case, from $2.37 to $4.34 per kg of synthetic fuel produced in the optimistic case, and from $15.21 to $26.36 per kg of synthetic fuel produced in the optimistic case. When the hydrogen was produced internally the prices increased by 5 - 10% in the expected case and by 16 - 22% in the optimistic case.

Figure 5.5 provides a breakdown of the cost of each factor contributing to the total cost.
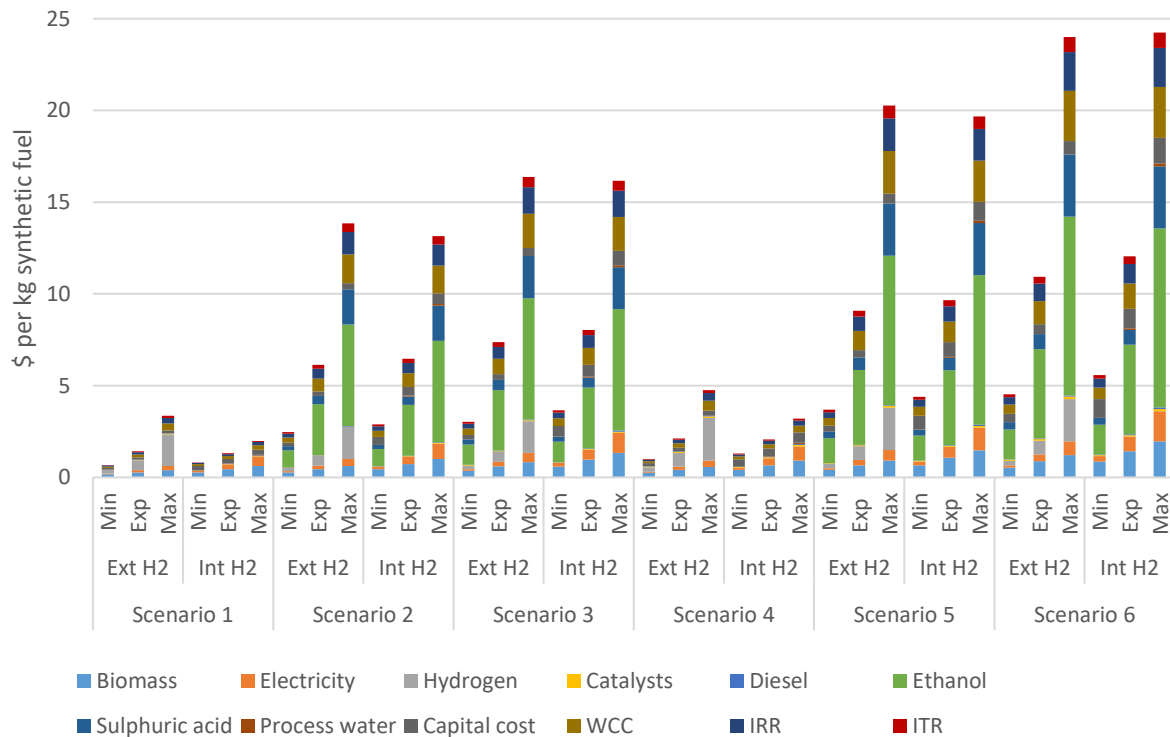
Figure 5.5: Minimum, Expected and Maximum fuel selling costs of the six scenarios and the breakdown of this cost

From Figure 5.5 it can be noticed that for Scenarios 1 & 4 the main contributors when hydrogen was acquired externally were hydrogen with 36 - 39%, and biomass with approximately 20% from the total price. For the internally produced hydrogen, biomass contributed approximately 19%, and electricity 33 - 35% of the total price. For Scenarios 2, 3, 5 & 6 ethanol was the main contributor, making up 41 - 47% of the total price. The sum of the working capital costs, internal rate of return and income tax rate made up approximately 25% of the total price. It can be remarked that the main contributors to the total price are: biomass, electricity, hydrogen, ethanol, sulphuric acid, capital cost, WCC, IRR and ITR. The other factors involved (catalysts, process water, diesel) only made up between 1 - 6% from the total price.

As ethanol has shown a great impact on the total price, the cheaper alternative of lignocellulose ethanol produced from corn stover was investigated. It was found that by using lignocellulosic ethanol, the total price of Scenarios 2, 3, 5, & 6 could be reduced to between $4.32 to $8.85 per kg of synthetic fuel produced in the expected case to $1.83 to $4.36 per kg of synthetic fuel produced in the optimistic case; and to $2.20 to

$19.92 per kg of synthetic fuel produced in the pessimistic case. This will reduce the minimum selling prices between 19 - 30 %.

5.4. Sensitivity analysis

It was noticed that the main factors affecting the selling cost are biomass, electricity, hydrogen, ethanol, sulphuric acid, capital cost, WCC, IRR and ITR. In addition to these items, process water for the reforming process was also considered for internal H_2 production, due to its high impact. These values were analysed further by looking at the Min, Exp and Max input values from Tables 4.1 - 4.8 (LCA chapter) and from Tables 5.2 and 5.3. The ITR, IRR, WCC and on-stream factor (days/year) were considered in alignment with Table 5.4. The synthetic fuel yield (see Figure 5.3) and therefore, Min, Exp and Max output values (output yield) from Tables 4.1 - 4.8 were also analysed.

The resulting diagrams for alternating each factor against the most likely value are presented in the Figure 5.6.

Figure 5.6 (a): Scenario 1 - Ext H_2
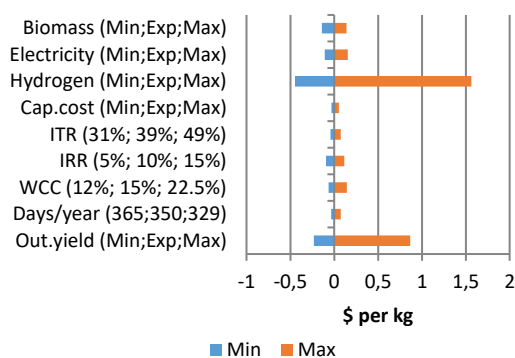
Figure 5.6 (b): Scenario 1 - Int H_2
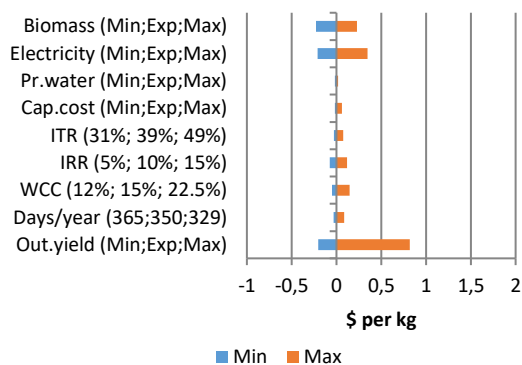
Figure 5.6 (c): Scenario 2 - Ext H₂
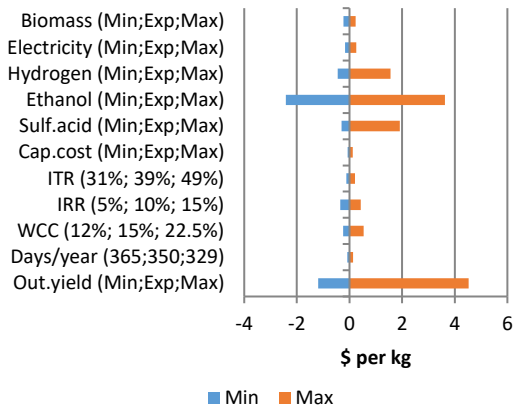
Figure 5.6 (d): Scenario 2 - Ext H₂
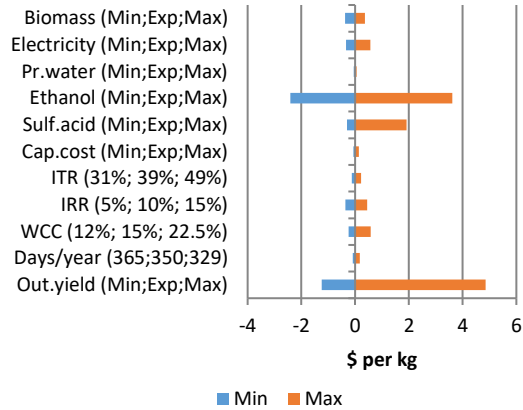
Figure 5.6 (e): Scenario 3 - Ext H₂
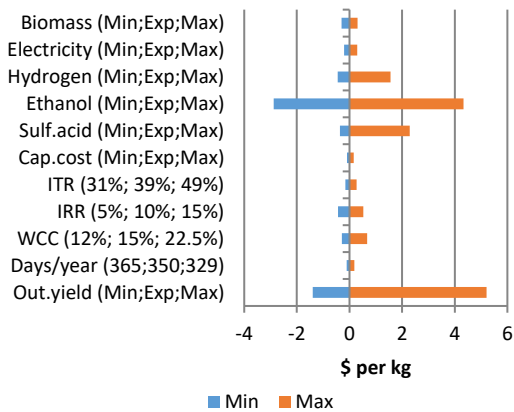
Figure 5.6 (f): Scenario 3 - Int H₂
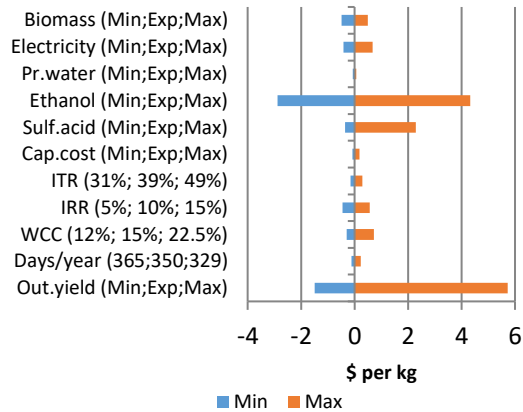
Figure 5.6 (g): Scenario 4 - Ext H₂
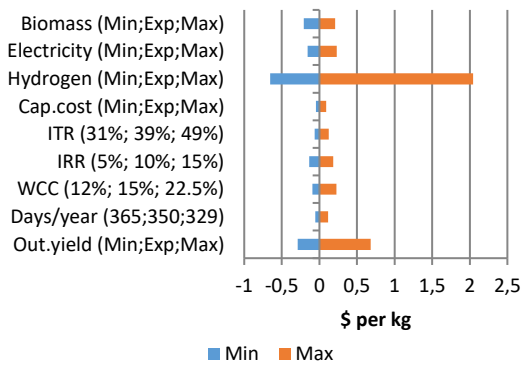
Figure 5.6 (h) Scenario 4 - Int H₂
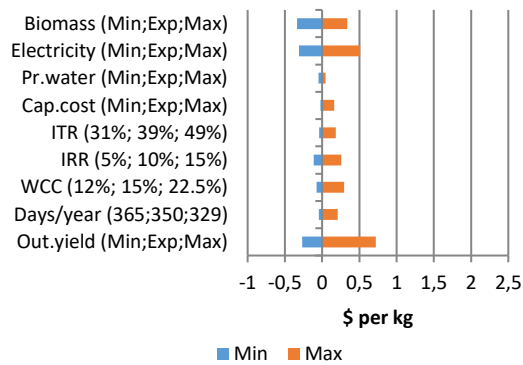
Figure 5.6 (i): Scenario 5 - Ext H$_2$
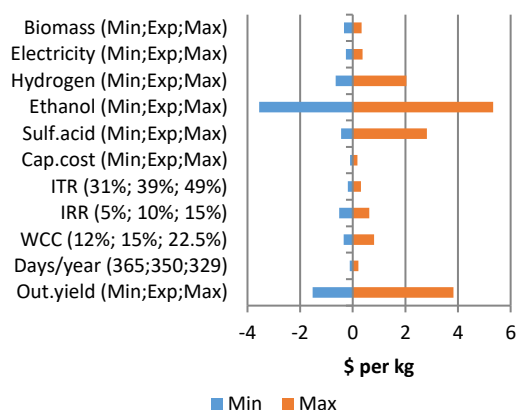
Figure 5.6 (j): Scenario 5 - Int H$_2$
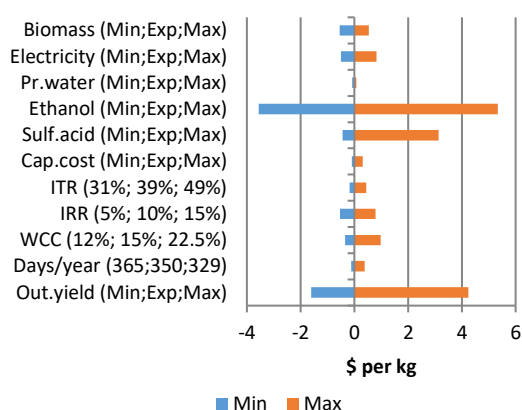
Figure 5.6 (k): Scenario 6 - Ext H$_2$
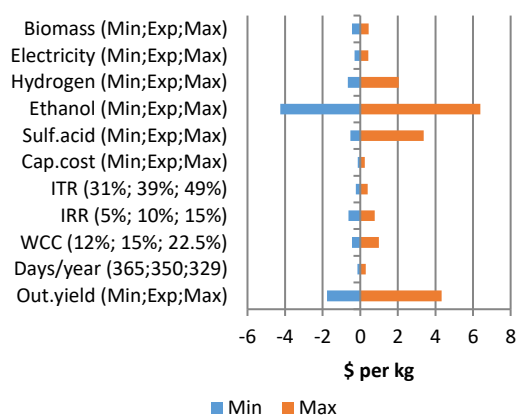
Figure 5.6 (l): Scenario 6 - Int H$_2$
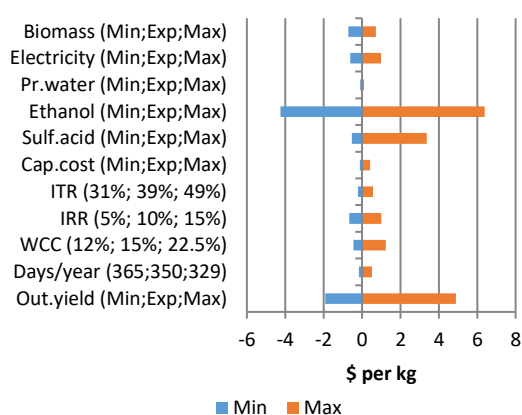
Figure 5.6(a-l): Sensitivity analysis of Scenarios 1 to 6, obtained by alternating each factor against the expected minimum selling cost of each scenario

From Figure 5.6 it can be noticed that in Scenario 1 & 4, when hydrogen was produced externally, the main factor in the total cost was hydrogen price. However, when the hydrogen was produced internally the main factors were electricity and biomass. The output yield showed a high impact for both hydrogen sources.

In Scenarios 2, 3, 5, & 6 the main factors in the total cost were the ethanol and sulphuric acid used in the esterification process, and the output yield. If the ethanol to bio-oil ratio is decreased from 2:1 to 1:1 (minimum possible) the price is decreased in these scenarios by approximately 40%; if the total price is improved, it can be decreased by 45 - 65%. Further research is needed to find cheaper and alternative catalysts to replace the sulphuric acid – to improve the esterification yield, when ethanol to bio-oil ratio is 1:1. Methanol (Sundqvist, Oasmaa and Koskinen, 2015) or dimethyl carbonate (Rekha *et al.*, 2009) may be more convenient for the economical perspective but they are not

sustainable from an environmental point of view. By assuming the most optimistic value for the whole system yield, a total reduction of 13 - 20% in the total costs is achieved. Furthermore, by optimising the whole system using lignocellulosic ethanol and assuming a tax exemption, the prices were found to be as low as $0.51 for Scenario 1 and up to $2.72 for Scenario 6.

The working capital cost, internal rate of return and income tax rate increased directly proportional to the total cost between the capital cost and operational cost. Therefore, an optimised capital and especially operational cost will decrease all the additional costs providing either a cheaper product or higher rate of return.

5.5. Conclusion

In this chapter, the costs of different scenarios to produce synthetic fuels were analysed. It was found that internal hydrogen production is beneficial only for Scenarios 1 & 4, if the processes were optimised, external hydrogen acquisition was found to be more convenient, due to the reduced hydrogen price and quantity needed for hydroprocessing. For the other four scenarios, external hydrogen purchase is favorable. Therefore, in the next chapter, only external hydrogen production will be considered.

The impact of each factor on the total price revealed that the hydrogen was the main factor contributing to the total cost of Scenarios 1&4, whereas ethanol was main influencing value in Scenarios 2, 3, 5 & 6. The best ways of improving Scenarios 2, 3, 5 & 6 is therefore to consider corn stover lignocellulosic ethanol as an alternative maize ethanol. Also, further research may be needed to find cheaper solvents or catalysts for the esterification process.

If the government were to provide programs for biofuel production, focused on cheaper renewable substitutes for ethanol, identification of better catalysts and methods by which the pyrolysis process could be powered by renewable sources, synthetic fuel could become financially viable in the future.

Chapter 6

6. Multi-Criteria Decision-Making in the Production of Synthetic Fuels

6.1. Introduction

Multi-criteria decision-making (MCDM) or Multi-criteria decision analysis (MCDA) deals with structuring and solving problems involving multiple criteria. Usually, there is not a unique solution for a problem and MCDM is designed to help differentiate between multiple potential solutions.

6.1.1. MCDM categories

In order to select the appropriate decision-making method for any type of problem it is important to understand the MCDM classification. A general classification of MCDM methods is presented in Figure 6.1.
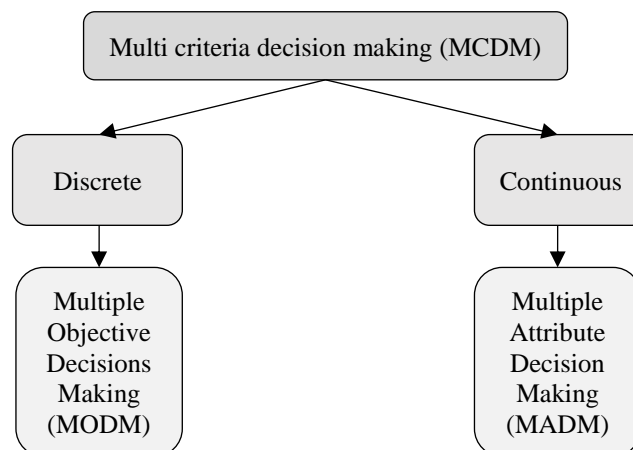
Figure 6.1: MCDM Category – based on data processing (Hwang and Masud, 2012)

Because for this thesis the possible answers are finite, results from the MADM category must be chosen. The finite possibilities entail a limited number of sub-criteria to be considered for each criterion. In MADM, a few alternatives have to be evaluated towards a set of criteria, which can be frequently difficult to quantify. The best

alternative is decided by making comparisons between alternatives in relation to each criterion.

6.1.2. MADM methods

There are various MADM methods: Weighted sum method (WSM), Weighted product method (WPM), Analytical hierarchy process (AHP), Technique for order preference by similarity to ideal solution (TOPSIS), Elimination et choice translating reality (ELECTRE), Preference ranking organization method for enrichment evaluation (PROMETHEE), etc. (J. Wang *et al.*, 2009). The methods can be sub-categorised as presented in the Figure 6.2.
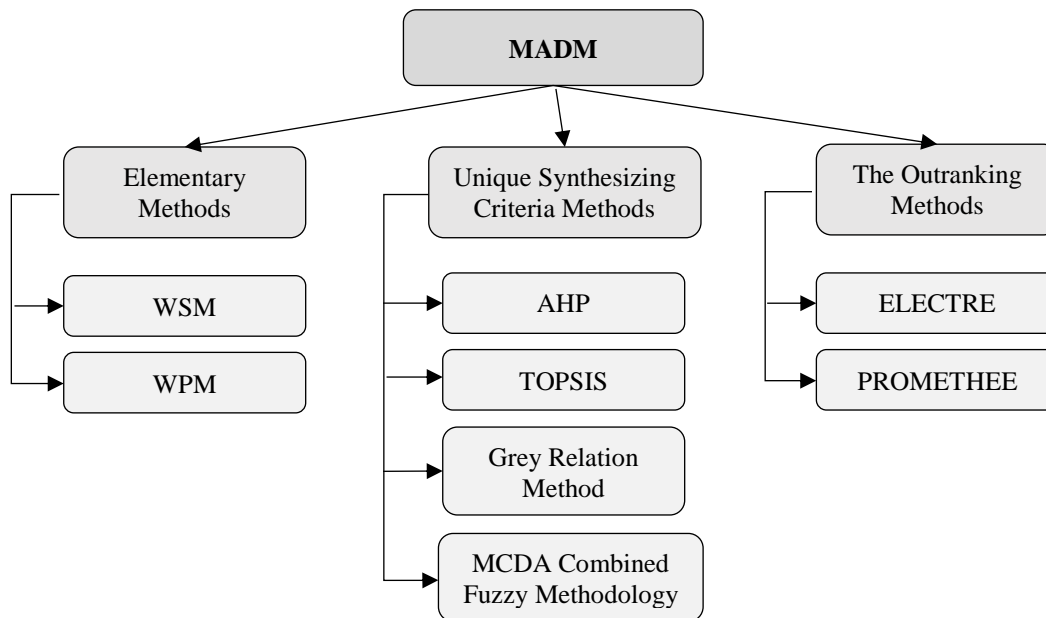
Figure 6.2: MADM methods if attribute data are available (Wang et al., 2009)

The MCDM process involves the following steps (Majumder, 2015):

1. Identifying the goal of the decision-making process; Selection of the Criteria / Sub-criteria; and Selection of the Alternatives.

2. Selection of the weighting methods to represent criterion importance (entropy and AHP).

3. Choose the appropriate MADM method (TOPSIS).

4. Decision-making based on the TOPSIS's results.

Mardani et al. (2015) reviewed the MCDM techniques and their applications between 2000 and 2014. They found that from a total of 393 papers, the method most used was

AHP accounting for 32.57% of the publications, and the second individual method was TOPSIS summing up to 11.4% (the hybrid MCDM and aggregation DM methods had 16.28%, respectively 11.7% imply more methods). Overall, the Unique Synthesizing Criteria Methods, AHP and TOPSIS were found to be the most utilised MCDM methods.

MCDM have become widespread in decision-making for sustainable structures because of multi-dimensionality of the sustainability goal and the complexity of technical and economic systems. Wang et al. (2009) carried out an extensive review on multi-criteria decision analysis for sustainable energy decision-making. The article reviewed the methods that can be used in different stages for criteria selection, criteria weighting and evaluation. The energy supply systems encompassed environmental, technical, economic and social criteria. The weighting methods were classified as subjective, objective and combined. Several methods were used to rank the results, including AHP and TOPSIS; and different aggregation methods were used to achieve the rational result in sustainable energy decision making. Çalışkan et al. (2013) reviewed the material selection for the tool holder using multi criteria decision making methods. To overcome the large material selection with specific properties and costs, numerous MCDM methods, including AHP, entropy and TOPSIS methods were used. The criteria weighting was performed using compromised weightings achieved by combining entropy and AHP methods. The materials were ranked and the best solution was chosen.

6.1.2.1. AHP method

The AHP method has been used as a decision-making tool in various domains. Bayazit (2005) used AHP for flexible manufacturing systems as a decision support tool in assessing the advanced manufacturing technologies. Most important factors in achieving the objective were found, and further sensitivity analysis were performed. Further, Bayazit and Karpak (2005) used AHP in vendor selection using both quantitative and qualitative criteria. They found that AHP can be used to manage complex problems, and also concluded that the sensitivity analysis is very important for practical decision-making, as it can help prioritise the criteria according to its impact on the whole system. Chang et al. (2007) used AHP in a manufacturing process by evaluating the outcomes they found the most precise slicing machine. Nixon et al. (2013) used AHP and HANP (Hierarchical Analytical Network Process) to evaluate

alternative technologies for generating electricity from municipal solid waste in India. ANP is an extension AHP that considers criteria interdependencies and therefore improves the model accuracy (T. L. Saaty, 1980). The technologies reviewed were: landfill, anaerobic digestion, incineration, palletisation and gasification; and they found anaerobic digestion to be the preferred technology. Yap and Nixon (2015) used AHP to find the best technology for energy recovery in India and UK. The technologies considered were mass burn incineration, refuse derived fuel incineration, gasification, anaerobic digestion and landfill gas recovery. As the two countries have different technical and socio-economical standards, it was found that anaerobic digestion was the best option for India, while gasification was the best option for UK. Singh et al. (2016) used AHP as a decision-making tool for flexible manufacturing. They aimed to adopt effective and efficient strategies, to fulfill customers' demands. The authors concluded that AHP is an effective decision-making method for multiple criteria analysis.

6.1.2.2. TOPSIS method

Shanian et al. (2006) reviewed the TOPSIS method for material selection of metallic bipolar plates for polymer electrolyte fuel cell. The weighting coefficients were obtained using an entropy method. Using this approach made it possible to draw up a list with all possible choices, from the best to the worst material. Li et al. (2011b) applied the TOPSIS method with entropy weight in safety evaluation of coalmines. They compared the safety conditions of four different mines. Chu et al. (2012) reviewed the application of TOPSIS method to select a suitable fixed seismic shelter for evacuation in case of an earthquake. A system with 3 first-level indices (criteria) and 9 second-level indices (sub-criteria) was used. The weightings indices were generating by using pair-wise (AHP) and entropy methods and the best selection was deducted by using the TOPSIS method. Zhang (2015) used TOPSIS method with the entropy weight for supplier evacuation of power grid enterprise, to ensure material demands were timely supplied.

6.2. Justification of MCDM criteria

To achieve the goal of the MCDM study, and find the best scenario for producing synthetic transportation fuels among the six upgrading scenarios outlined in chapter 2, several criteria are established using the data gathered in Chapters 4 and 5.

6.2.1. Environmental criteria

The environment criteria were found by simulating a database achieved from literature review and own calculations, by means of the GaBi Professional software (Vienescu et al. 2017). The transportation sector accounted for over 14% of the total global CO_2 emissions, and annual emissions are still increasing every year (EPA, 2017a). Therefore, finding the CO_2 emission levels was the main aim of the environment assessment. Several other criteria were included to consider fertilisers implications (Iribarren *et al.*, 2012), specifically acidification and eutrophication.

6.2.2. Technical criteria

Several technical criteria are included into the decision rationale to take into account that pyrolysis oils needs to be improved before they can be used to replace fossil fuels. The key technical criteria chosen for this study were acidity, oxygen content and viscosity.

Bio-oil produced from biomass normally has a high oxygen content (20 - 50wt %) and acidity (pH = 2.5 - 3), resulting in a low heating value (16-18 MJ/kg), high viscosity and corrosiveness (Milina *et al.*, 2014; Gunawan *et al.*, 2012).Hydrotreating pyrolysis oils obtained from corn stover using an Ru/C catalyst can achieve a 25 - 26 wt% oxygenated product (Capunitan and Capareda, 2014). Oxygen content after one step hydrotreating was found to decrease from around 40 % to 18 - 27 wt% (Wildschut, 2009; H. Wang *et al.*, 2013). The amount of deoxygenation after two step hydrotreating can be as low as 2 wt% (Han *et al.*, 2011), but 6 - 11 wt% is more likely (H. Wang *et al.*, 2013; Wildschut *et al.*, 2009).

The viscosity of hydrodeoxygenated bio-oil was found to be between 1.0 and 4.6 cP (G. W. Huber *et al.*, 2006) and using esterification the bio-oil can be further improved. (Ciddor *et al.*, 2015). Viscosity is a decreasing function of the oxygen content (Wildschut, 2009) and is assumed to be directly proportional to it.

The acidity was found, for mild and two stage hydrodeoxygenation, to have pH values between 5 and 6 (D. C. Elliott, 2007; Wildschut, 2009), and esterification improves the pH value to between 6 - 8 (Sundqvist *et al.*, 2015). The synthetic route for the conversion of acetic acid to propanone represents an efficient method for removing 3 atoms of O at the cost of only one C. This changes the O/C (w/w) ratio from 53% to

27%, at the cost of reducing the mass of 'combustible' acid by approximately 50% (J. Wang, Chang and Fan, 2010). Ketonisation results in a reduction of approximately 50% in O/C, but as acids account on average for only 20% this only represents a 10% reduction (Y. Zhang *et al.*, 2017).

6.2.2.3. Economic criteria

The cost of biofuels in comparison with gasoline and diesel have been previously calculated (S. B. Jones *et al.*, 2009; Wright *et al.*, 2010b; S. Jones *et al.*, 2013), but the cost of more complex biofuels have not. Hence, the economic data for the six scenarios was calculated in Chapter 5. The plant capacity for all scenarios was considered to be 2000 metric tons of dry corn stover per day. Equipment sizing and capital cost of fast pyrolysis process and hydroprocessing were taken from the literature review (S. B. Jones *et al.*, 2009; Wright *et al.*, 2010b; S. Jones *et al.*, 2013; Y. Zhang *et al.*, 2013). The capital cost for esterification and ketonisation were calculated using online price estimates. The operational cost was calculated by using the variable operational costs, such as raw materials (corn stover), utilities costs (electricity) and operating material costs (catalysts, ethanol); and the fixed operational costs such as salaries and maintenance, which were taken from literature review. Using all the data, expected and the minimum costs to produce one kilogram of synthetic fuel for each scenario was calculated; the (minimum) selling price of one kilogram of synthetic fuel produced from each scenario was calculated based on the expected and the minimum costs achieved by adding the capital and operational costs, an income tax rate of 31 - 39%, a working capital costs of 12 - 15% (Y. Zhang *et al.*, 2013), and an internal rate of return of 10% (Wright *et al.*, 2010b; S. Jones *et al.*, 2013; Y. Zhang *et al.*, 2013). An outcome from the work performed in Chapter 5 is that the key financial criteria to use an MCDM to compare upgraded synthetic fuels are capital cost, operational cost and selling price.

6.2.3. MCDM table

The environmental, technical and economic criteria, and associated expected, minimum and maximum possible values for each upgrading scenario, are summarised in Table 6.1. This table of information is used to enable the performance of each alternative scenario to be assessed against each criterion.

Table 6.1: MCDM table

Criteria	Alternatives	Unit	Value	Sc. 1	Sc.2	Sc.3	Sc.4	Sc.5	Sc.6	Refs:
Environment	Global warming potential	gCO_2 / kg of bio-oil	Exp	-972	-2039	-2779	-1509	-3126	-4126	see Chapter 4
			Min	-1355	-2406	-3196	-2175	-3781	-4980	
			Max	-2831	-5996	-7796	-4164	-8227	-10628	
	Acidification	kg SO_2 eq. [E-03]	Exp	4.95	9.78	18	7.18	14	27	see Chapter 4
			Min	2.8	4.88	12	4.04	7.22	17	
			Max	12	24	40	14	28	48	
	Eutrophication	kg PO_4^{3-} eq. [E-03]	Exp	1.01	2.61	3.34	1.47	3.57	4.91	see Chapter 4
			Min	0.62	1.26	1.84	0.92	1.9	2.78	
			Max	2.15	5.94	7.74	2.53	7.08	9.25	
Financial	Capital cost	£ / kg synthetic fuel prod.	Exp	0.11	0.22	0.30	0.19	0.38	0.51	see Chapter 5
			Min	0.09	0.17	0.23	0.16	0.31	0.41	
			Max	0.15	0.30	0.41	0.26	0.51	0.68	
	Operational Costs	£ / kg synthetic fuel prod.	Exp	0.97	4.44	5.31	1.41	6.53	7.80	see Chapter 5
			Min	0.42	1.70	2.06	0.59	2.48	3.01	
			Max	2.40	10.25	12.06	3.36	14.92	17.59	
	Selling price	£ / kg synthetic fuel prod.	Exp	1.42	6.13	7.37	2.12	9.09	10.94	see Chapter 5
			Min	0.64	2.37	2.90	0.96	3.54	4.34	
			Max	3.68	15.1	17.97	5.23	22.24	26.36	
Technical	-Oxygen content;	%		18 - 27	8 - 16	6 - 12	6 - 11	4 - 10	1 - 9	Assumed from: (Y. Zhang *et al.*, 2017; J. Wang *et al.*, 2010; Wildschut *et al.*, 2009; D. C. Elliott *et al.*, 2009; D. Elliott and Neuenschwander, 1997)
	-Viscosity;	cP		1 - 4.6	2 - 2.4	1.9 - 2.2	1 - 4.6	2 - 2.4	1.9 - 2.2	Assumed from: (Ciddor *et al.*, 2015; J. Wang *et al.*, 2010; G. W. Huber *et al.*, 2006)
	-Acidity;	pH		5	6 - 8	6 - 8	5.8,6 - 6.5	6 - 8	6 - 8	Assumed from: (Y. Zhang *et al.*, 2017; Sundqvist *et al.*, 2015; Wildschut, 2009; D. C. Elliott, 2007)

6.3. Results and discussion

To quantify the importance of each criteria and sub-criteria, a survey was carried out with experts in the field scoring each criteria and sub-criteria with values between 1 (less important) and 9 (most important), see Appendix 2. Using the survey results, a hierarchical framework for selecting the best technological process to produce transportation fuels is represented in Figure 6.3. Whilst each criterion was given a similar weighting of importance, the environmental criteria were weighted lower at 0.26, whereas economic and technical criteria had an equal importance on 0.37, as determined by the panel of experts.
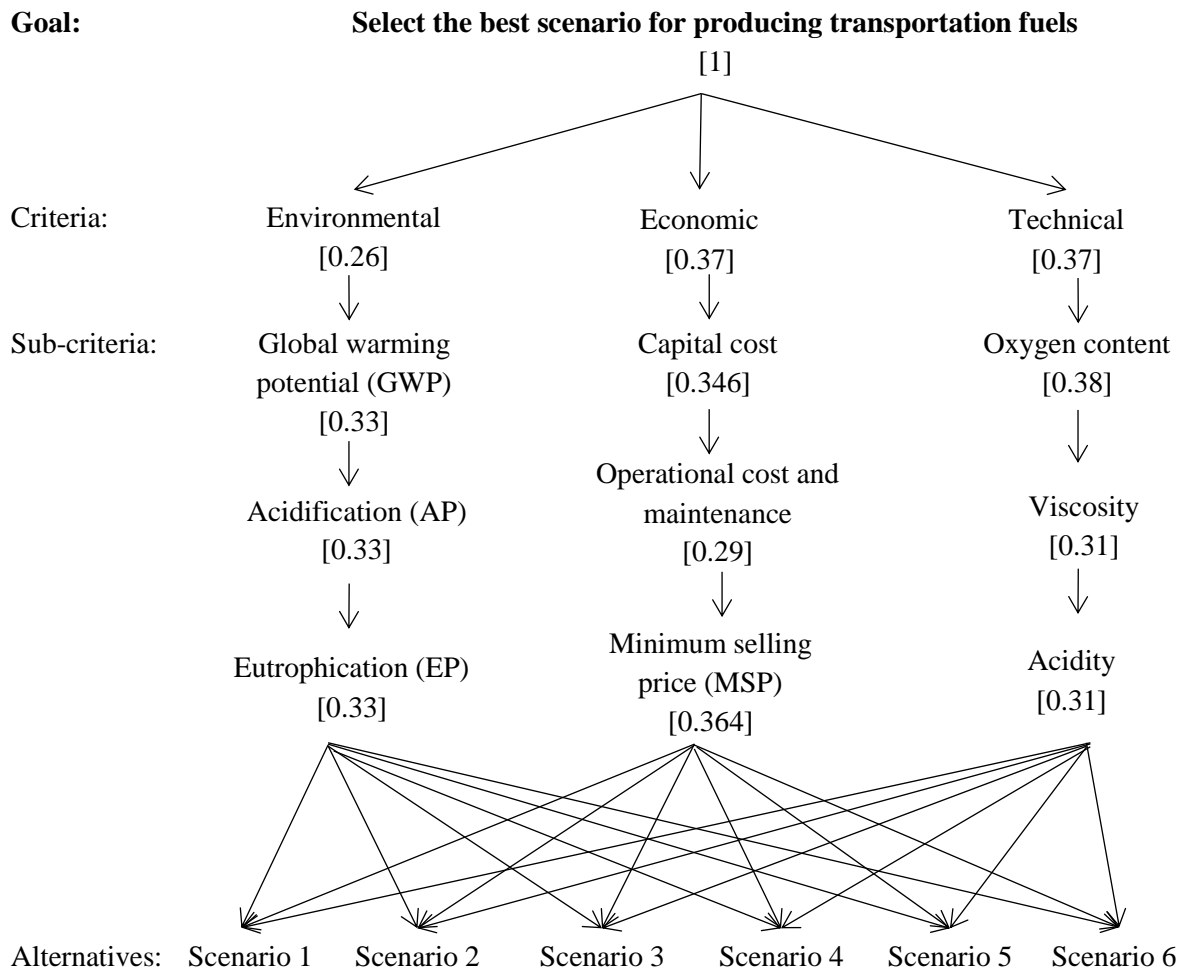
Figure 6.3: AHP – hierarchical framework for selecting the best technological process to produce transportation fuels

By using the pair-wise method (see AHP hierarchical framework), entropy method and compromised method (between the previous two) different weightings for each sub-criteria were obtained and are presented in Table 6.2. The entropy and compromised weightings were further used for TOPSIS method.

Table 6.2: Pair-wise, entropy and compromised weightings used

Criteria / Weight	GWP	AP	EP	Cap. cost	Oper. cost	MSP	Oxygen cont.	Visco-sity	Aci-dity
Pair-wise weights	0.0877	0.0877	0.0877	0.1273	0.1072	0.1339	0.1417	0.1134	0.1134
Entropy weights	0.1640	0.0513	0.0942	0.0726	0.1745	0.1655	0.0151	0.2587	0.0042
Compr. weights	0.1317	0.0412	0.0757	0.0846	0.1713	0.2030	0.0195	0.2686	0.0044

6.3.1. Decision-Making based on MCDM results

The AHP method used the subjective weightings found through conducting the survey; the weightings were calculated as an average of the survey values (see Figure 6.3). Because of the objective method of obtaining the normalised weightings, TOPSIS method with entropy weights have unique values, dependent on the degree of disorder in the criteria values. TOPSIS used two different weighting methods: entropy method (objective) and compromised method (combined subjecting method with the objective method). All three methods were conducted considering the minimum, expected and maximum possible values (see Table 6.1) and the results are listed in the Figure 6.4 below:
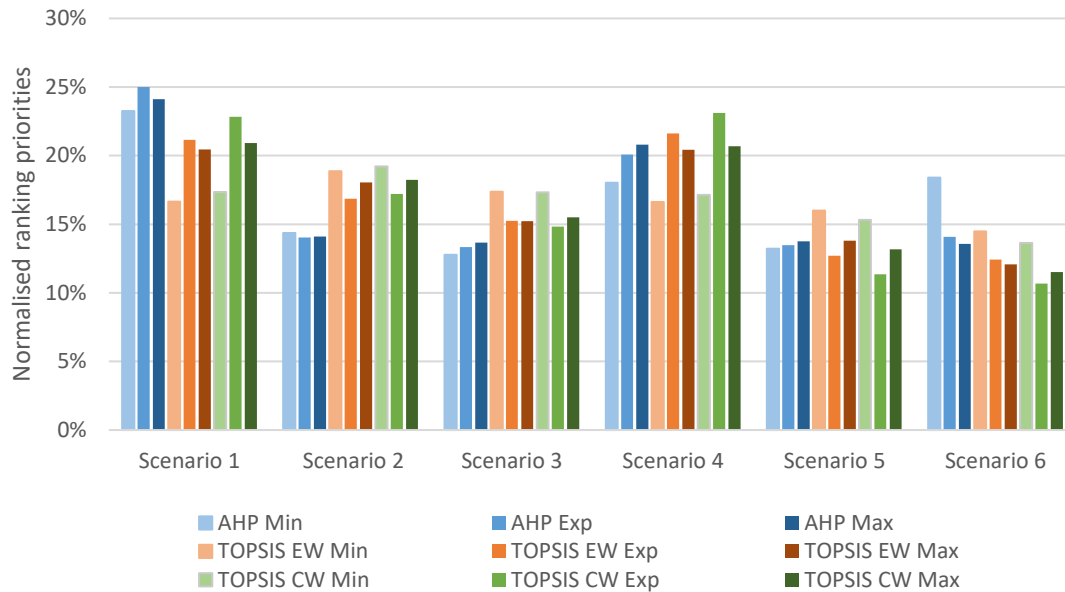
Figure 6.4: Normalised ranking priorities for AHP, TOPSIS with entropy weightings & TOPSIS with compromised weightings methods for minimum, expected and maximum values, showing the preference of each scenario for producing transportation fuels

From Figure 6.4 it can be noticed that by using an AHP method, with the subjective weightings (AHP), Scenario 1 was the preferred option and Scenario 4 the second option for the expected (Exp) and pessimistic (Max) values. When optimistic scenario performance inputs were used (see Min values in Table 6.1), Scenario 1 was still the preferred option, but it was followed by Scenario 6. By using TOPSIS method with the entropy objective weightings (TOPSIS EW.), Scenario 1 and Scenario 4 were the preferred options for the expected (Exp) and pessimistic (Max) values. In the most optimistic cases (Min), Scenario 2 and Scenario 3 were the best options. By using TOPSIS method with the compromised weightings (TOPSIS CW.), Scenarios 1 and 4 were the preferred options for the expected (Exp) and pessimistic (Max) values. When the optimistic inputs (Min) were used, Scenario 2 was found to be the preferred option, followed by similar values of Scenarios 1, 3 & 4.

Borda and Coperland were the two aggregation voting methods used to obtain the final ranking of the entire system. By using the weighted rankings from all the MCDM methods - AHP, TOPSIS with entropy weights and TOPSIS with compromised - the aggregation normalised rankings were obtained and are shown in Figure 6.5.

Figure 6.5 (a): Optimistic (min) values
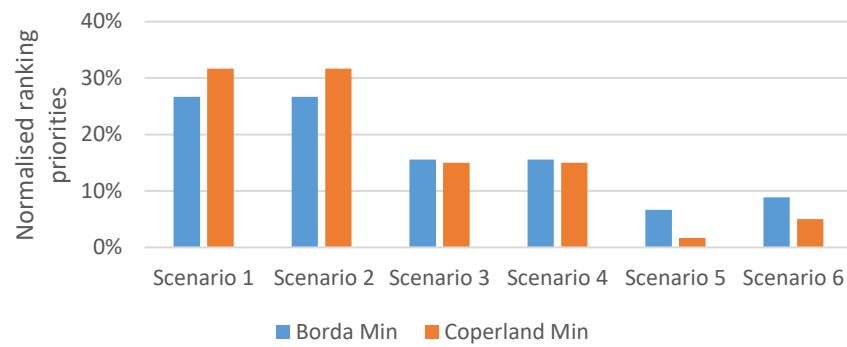
Figure 6.5 (b): Expected (exp) values
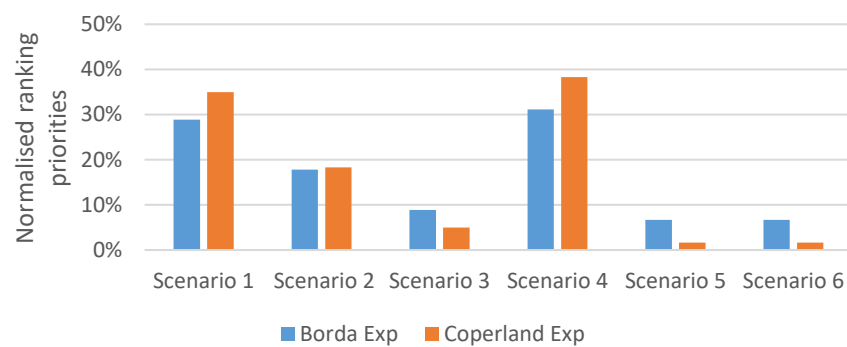
Figure 6.5 (c): Maximum (max) values
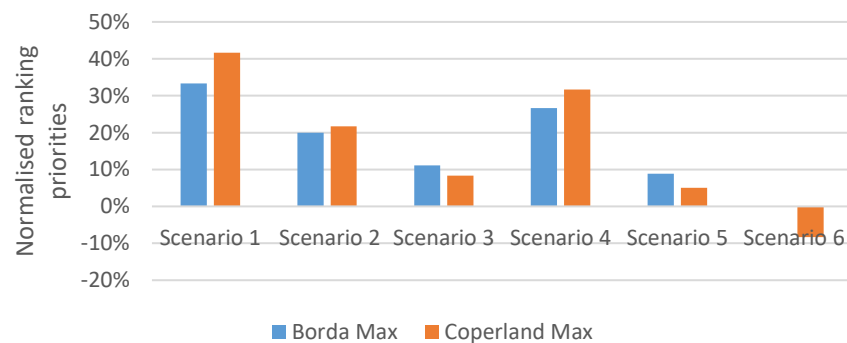
Figure 6.5(a-c): Normalised ranking priorities for Borda and Coperland voting methods, for minimum (a), expected (b) and maximum (c) values, showing the preference of each scenario for producing transportation fuels

From Figure 6.5 it can be noticed that by using both aggregation methods the ranking order of the scenarios 1 to 6 is the same. Comparing the most optimistic, expected and pessimistic values, the scenario ranking changed. For expected and pessimistic values Scenarios 1 & 4 were preferred, followed by the Scenarios 2 and 3; for the most optimistic values Scenarios 1 and 2 were preferred, followed by Scenarios 3 & 4.

The aggregation method was also used to normalise the rankings for minimum values (see Figure 6.5a assumptions) with optimised biomass to synthetic fuel yield outputs (see Figures 5.3 and 5.6) and assumed tax redemption, see Figure 6.6.
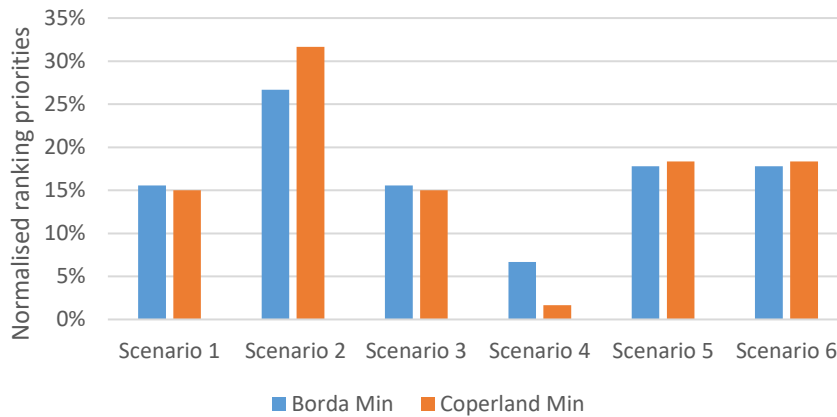
Figure 6.6: Normalised ranking priorities for Borda and Coperland voting methods, for most optimistic possible scenarios with optimised output yields, showing the preference of each scenario for producing transportation fuels.

Figure 6.6 shows the normalised ranking priorities in the most optimistic case scenarios, when all inputs and outputs were optimised and including anticipated governmental measures for tax redemption. Scenario 2 was still preferred, while Scenarios 5 and 6 were the almost joint second most promising. However, this assumes minimum inputs and maximum outputs for the whole system. This might not be very likely, but is achievable in the future by means of future technological improvements.

The aggregation method is a well-known practice to identify best rankings. The most optimistic situations indicated equal rankings, placing Scenarios 1 and 2 on top, followed by Scenarios 3 and 4. In the light of this, a sensitivity study is performed to find the preferred options. As the purpose of the sensitivity study is to find the best option, the pessimistic scenarios were not considered further.

6.3.2. Sensitivity analysis

Due to the limited number of experts answering the survey, and for a better understanding on how different criteria may influence the final ranking, it was decided to carry out a sensitivity analysis for the AHP method; this was performed by

alternating the criteria weightings. The Environmental, Economic and Technical criteria weightings were varied by choosing: average values (obtained from different participants' opinions - on a scale from 1 to 9), equal values (by assuming all three criteria have equal values), and by alternating the most important criteria on a scale from 1 to 9 as follows: environmental most important, economic and technical less important (Sensitiv 1), economic most important, environmental and technical less important (Sensitiv 2), technical most important, environmental and economic less important (Sensitiv 3). The normalised ranking priorities of the six scenarios (for expected and optimistic values) with the varying values are illustrated in Figure 6.7. The purpose of the sensitivity analysis was to optimise the system and find the best option, therefore maximum (the most unlikely) scenarios were not considered further due to the high feedstock usage (7.29 - 20.6 kg/kg synthetic fuel compared to 3.87 - 12.2 kg/kg synthetic fuel in the expected case and 3.03 - 9.53 kg/kg synthetic fuel in the most optimistic case) and the extremely high cost impacts (see Table 6.1) – which were considered not to be compatible with the fossil fuels.
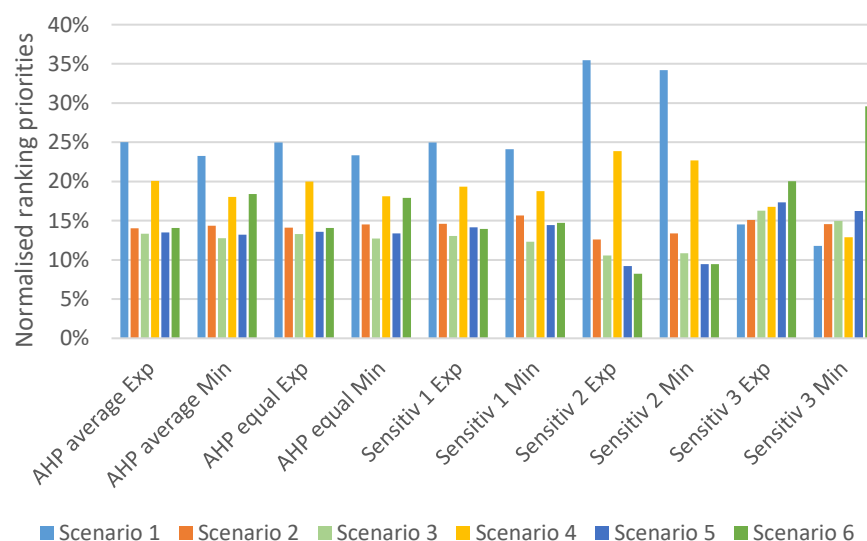
Figure 6.7: AHP method - Sensitivity graph for average weightings, equal weightings, highest weightings: environmental (Sensitiv 1), economic (Sensitiv 2) and technical (Sensitive 3) - showing the six different scenarios rankings for both expected (Exp) and optimistic (Min) values

From Figure 6.7 it can be noticed that the rankings of the six scenarios, delivered by using survey participants' (average values) were very similar with the ranking provided by using equal values between the criteria. In both cases Scenario 1 and 4 were

preferred for the expected values, with approximately 25% and 20% respectively; and Scenarios 1 and 6 were preferred for the optimistic values, with approximately 23% and 18% respectively. Even if from the figure some values look to be the same, they are slightly different, e.g. for expected values - Scenario 1 acquire a share of 24.932% from average criteria values and 24,933% from equal criteria values. Similarly, when the environmental criterion was considered the most important criteria (Sensitiv1), the results did not significantly change for the expected values, as Scenario 1 and 4 remained the preferred options, with similar percentages. However, for the optimistic values Scenarios 4 was the second option (with approximately 19%), and Scenario 6 dropped to fourth place (with only approximately 15%), unlike for the previous criteria values. In contrast, it can be noticed that when economic criterion was the most important Scenarios 1 and 4 ranking priorities increased, for both expected and optimistic values to between 33 - 35% and 22 - 24%, respectively. When technical criterion was the most important, Scenarios 5 and 6 were preferred, for both expected and optimistic values with values between 16 - 30%. It can be seen that when the technical criterion is considered to be the most important criterion and when the most optimistic case is considered, Scenario 6 is shown to be the preferred option. However, the experts considered that a balance between environmental, cost and technical criterion would be more beneficial than the highest fuel quality.

Similar with the sensitivity analysis for AHP method (above), sensitivity analysis for the TOPSIS method with compromised weightings was further performed by interchanging the same criteria values. The compromised weightings were calculated by using the objective entropy weightings and subjective pair-wise weightings (see AHP hierarchical framework). The same five criteria value options were considered as for AHP method: average values, equal values, Sensitiv 1, Sensitiv 2 and Sensitiv 3. The normalised ranking priorities of the six scenarios (for expected and optimistic values) with the varied values are illustrated in Figure 6.8.
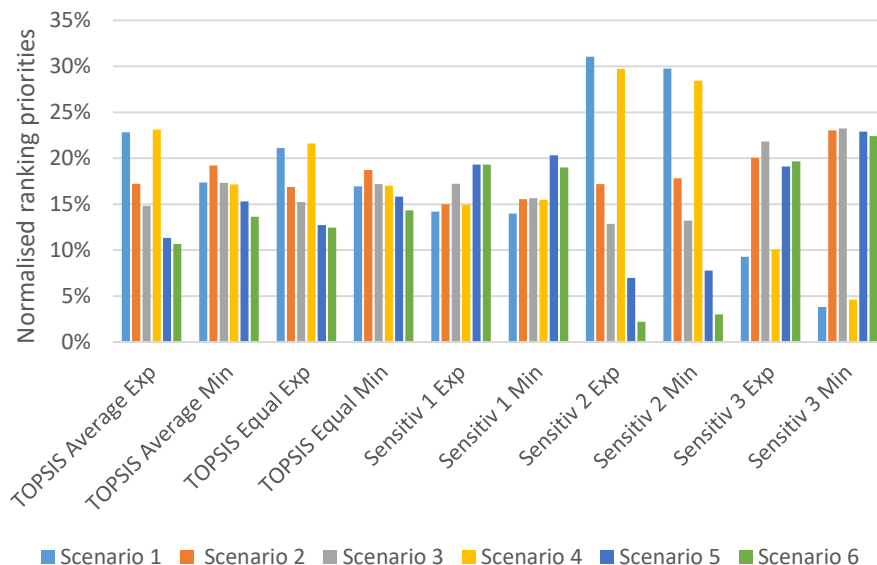
Figure 6.8: TOPSIS method with compromised weightings (CW) - Sensitivity graph for average weightings, equal weightings, highest weightings: environmental (Sensitiv 1), economic (Sensitiv 2) and technical (Sensitiv 3) - showing the six different scenarios rankings for both expected (Exp) and optimistic (Min) values

From Figure 6.8, it can be seen that, similar to the AHP method, the rankings of the six scenarios that resulted from using survey participants' (average values) were very similar with the ranking resulted by using equal values between the criteria. In both cases, Scenario 1 and 4 were preferred for the expected values, with approximately 19%; and Scenarios 2 and 3 were preferred for the optimistic values, with approximately 20% and 18%. When the environmental criterion was considered the most important criteria (Sensitiv1), the results showed that Scenarios 5 and 6 were preferred for both expected and optimistic values, between 19 - 20% and 22 - 24%, respectively. In contrast, it can be seen that, similar to the AHP method, when the economic criteria were the most important, Scenarios 1 and 4 were most preferred for both expected and optimistic values, to between 29 - 31% and 27 - 28% respectively. When the technical criteria were the most important, Scenarios 2 and 3 were preferred, for both expected and optimistic values with values of approximately 23%; but they were closely followed by Scenarios 5 and 6 (with values between 22 - 23%), especially in the most optimistic circumstances. By analysing this figure, it was noticeable that if the environmental criteria were considered to be the most important criteria, Scenarios 5 and 6 would be the preferred scenarios. If the technological criteria were the most important then Scenarios 2, 3, 5, and 6 would be equally preferred, while Scenarios 1

and 4 were less preferable. Therefore, due to the high cost involved in each additional process, Scenarios 1 and 4 arose to be preferable – from experts' opinions - in the most expected situations; while in fact the synthetic fuels obtained from these scenarios do not meet the necessary technical conditions as sustainable drop-in fuels.

6.4. Conclusions

The MCDM results showed that Scenarios 1 and 4 are the preferred options in the expected and pessimistic circumstances, but if the system is improved enabling the optimised values to be obtained, Scenarios 2 and 3 were shown to be promising options (see Figure 6.5a-c).

The sensitivity analysis showed that when using an AHP method Scenarios 1 and 4 were the preferred options in the most expected cases, for most criteria variations, but in some most optimistic cases Scenario 6 came out as a promising option (see Figure 6.7). An exception was when the technical criteria were considered to be the most important Scenarios 6 & 5 were the preferred options for both expected and optimistic situations.

By carrying out a sensitivity analysis on TOPSIS with combined weightings result (see Figure 6.8), it was found that Scenarios 1 and 4 were the preferred options only for average criteria values (survey participants' opinions) and when the criteria weighting were considered to be equal – in the most expected cases; and when economic criterion was considered the most important (Sensitiv 2) – in both most expected and optimistic cases. Scenarios 2 and 3 were found to be the most preferred options for the most optimistic cases, when average criteria values and equal criteria values were considered; but also when technical criterion was considered the most important (Sensitiv 3). Scenarios 5 and 6 were shown to be the most preferred options when the environmental criterion was considered to be the most important (Sensitiv 1); but also shown high rankings when the technical criterion was considered to be the most important (Sensitiv 3).

For the AHP method, it can be noticed that from the environmental and technical perspective, Scenarios 2, 3, 5 & 6 are feasible, but because of the high costs involved in the esterification process Scenario 1 & 4 were better options in the most expected

circumstances. On the other hand, in the most optimistic cases Scenario 6 was the second best option from the technical point of view (see Figure 6.7). For the TOPSIS method with compromised weightings Scenarios 2, 3, 5 & 6 were the most favorable from an environmental and technical perspective, but Scenarios 1 & 4 are preferred considering the costs involved (see Figure 6.8).

From both the sensitivity study and aggregation method, Scenarios 2 and 3 were identified as providing reasonable trade-offs between product quality, cost and possible environmental benefits.

Chapter 7

7. Conclusion

7.1. Introduction

This concluding chapter's goal is to summarise and evaluate the whole thesis outcomes, considering the previous aim and objectives outlined in Section 1.2. Each objective is individually evaluated in order to examine the extent to which they were achieved, and the overall thesis aim is further assessed. The chapter ends with recommendation for further work.

7.2. Responses to objectives

Objective 1. Identify promising options for thermochemical conversion of waste biomass into a synthetic fuel

This objective was achieved by conducting an intensive literature review in the field of synthetic fuels and thermochemical conversion technologies. The literature review was used to identify promising scenarios for producing synthetic fuels from waste biomass to be further analysed. Various aspects were studied to establish the best alternatives to convert waste biomass into a synthetic transportation biofuel: different types of biomass were reviewed to find the feedstock representing waste biomass, pyrolysis reactors were investigated to find which one would be the most appropriate to use, different bio-oil upgrading methods were considered and revised in order to recommend the most promising upgrading methods of bio-oil to synthetic fuels. Six alternatives were identified as an outcome from the literature review: i) hydrotreating and hydrocracking; ii) esterification, hydrotreating and hydrocracking; iii) esterification/ketonisation, hydrotreating and hydrocracking; iv) two-stage hydrotreating and hydrocracking; v) esterification, two-stage hydrotreating and hydrocracking, and vi) esterification/ketonisation, two-stage hydrotreating and hydrocracking. Scenarios 1, 2, 4 and 5 were selected based on existing thermochemical upgrading technologies, whilst scenarios 3 and 6 were suggested in order to advance synthetic fuels with improved properties. As an extension of these scenarios, other processes such as biomass

torrefaction, liquefaction or gasification could be used in the process of obtaining synthetic fuels for the transport industry. Due to the literature review outcome showing low liquid yields they were not considered in this study. A method to obtain higher quality pyrolysis oil was through catalytic pyrolysis, but it was also not considered because of lower liquid yields; however, further work may consider improving its yield.

The contribution to the knowledge of the first objective is:

- Comparison of new and emerging designs for upgrading pyrolysis bio-oils

Objective 2. Evaluate the environmental impacts of different processes for producing alternative synthetic fuels in comparison to conventional transportation fuels

The first step in meeting this objective was to find appropriate means and methods to evaluate the environmental sustainability of the six different pathways to produce synthetic fuels, in Chapter 3. The life cycle assessment framework was set accordingly to ISO 14040 and ISO 14044 standards. Standard LCA methodology was applied and therefore mass allocation was used for a well-to-wheel system boundary. Other allocation method, such as energy allocation, could have been considered; yet for the purpose of this study and according to previous research, mass allocation was preferred. Chapter 4 looked into producing drop-in fuels by upgrading fast pyrolysis bio-oil through the six different scenarios. The bio-oil was obtained by using the conventional pyrolysis steps: feedstock selection, feedstock pre-treatment and the pyrolysis process. Corn-stover was chosen as a favorable feedstock due to feedstock data availability. Other feedstocks besides corn-stover and wood should also be considered in further work. For the present LCA study on corn stover, an allocation approach based on nutrient replacement was used.

The fluidised bed reactor was considered to be the most suitable for the pyrolysis process due to a relatively simple design, ease of operation, good temperature control and suitability for large scale plant and high liquid yield. However, improving the pyrolysis reactor to achieve higher quality fuel properties, through designing new filtration systems for better char removal or improving the solid residence time, may be worthy of further consideration.

Simulations of pyrolysis oil production and upgrading to each of the six scenarios were developed in GaBi Professional software. The inventory analysis was carried out based on a broad database obtained through literature review, existing LCA databases and calculations. The LCA data available in literature was often inconsistent and lacked transparency. Therefore, primary data from existing companies would improve the model, but this data is still difficult to obtain due to the immaturity of the technology.

Each scenario was evaluated and interpreted by using the CML2001 impact assessment method – in accordance with European standards. However, ILCD recommendations can be further used to analyse other impacts (such as human toxicity cancer and non-cancer effects, particulate matter, ionizing radiations, etc.). Different sources for hydrogen production were also analysed, and two of them were considered to be sustainable: external hydrogen production from natural gas and internal hydrogen production from pyrolysis aqueous phase. Therefore, for the next objective all six scenarios with both hydrogen production sources were considered.

For the second objective the contribution to the knowledge are:
- New data on the environmental impacts of synthetic fuels produced from pyrolysis oils
- LCA results revealing how synthetic fuels could be more damaging to the environment than fossil fuels, which is a very significant finding.
- New emerging pyrolysis oil upgrading methods evaluated and possible ranges in life cycle assessment inventory data, which have not been analysed before
- Computational simulations of the data of different hydrogen sources in the process of producing synthetic fuels - to find which source results in less environmental impact

Objective 3. Assess the techno-economic feasibility of the different processes for producing synthetic fuels for transport industry

This objective was accomplished by implementing a financial study for the chosen pathways to produce synthetic fuels. In Chapter 5 the synthetic fuel, produced through each of the six scenarios considering both hydrogen sources, price was assessed. The minimum selling price of one kilogram of synthetic fuel was calculated based on the capital cost, operational cost, on-stream factor (plant functionality each year), and other

costs and taxes as working capital cost (WCC), internal rate of return (IRR) and income tax rate (ITR) totalised 25% of the total cost. Therefore, policies to reduce the cost of biofuels production are needed. It was shown that the synthetic fuel price was influenced by high esterification costs. By optimising the whole system, using lignocellulosic ethanol and tax exemption the prices could be as low as $0.51 for Scenario 1 and up to $2.72 for Scenario 6. If the hydrogen was produced internally the costs increased by 5 - 9% in the expected case and by 14 - 19% in the optimistic case. Therefore, to further progress this objective just the external hydrogen production was taken into consideration. This objective was achieved using secondary data and self-calculated data through cost estimation, therefore further research may be carried out by using primary data – which may be beneficial especially if it provides more accurate capital costs, as well as raw materials, energy and taxation local costs. When the most optimistic biomass to synthetic fuel yields were considered, the operational costs showed a decrease of 16 - 20%, due to less feedstock having to be collected, transported and processed. Therefore, more work should be done to improve bio-oil production, esterification and HDO processes output yields; this can be done by improved reactor designs and catalysts. Further work should also be carried out to forecast the costs of the six scenarios for the next 30 years, by forecasting all the materials and energy costs but also the possible improvement in the technological processes and comparison with forecasted fossil transportation fuels prices.

The contribution to the knowledge of the third objective is:

- An economic appraisal of a range of bio-oil upgrading method to establish feasible selling prices

Objective 4. Design a multi criteria system to assess the feasibility of different processes for producing synthetic fuels.

This objective was achieved by designing a table with the environmental, financial and technical criteria of the six different pathways to produce synthetic fuels, and by performing several multi-criteria decision analysis on the acquired data. A drawback regarding the data considered is that just a limited number of sub-criteria were considered for each criterion. Further research may be carried out to analyse how using various sub-criteria may influence the results. For the present LCA study, acidification

and eutrophication were considered the most important environmental impacts beside CO_2 emissions (GWP), due to the fertilisers usage; if other feedstock would be used, other environmental impacts might be preferable. For the economic impact capital cost, operational cost and the minimum selling price were considered; however, other sub-criteria such as local taxes may be considered. For the technical criteria, oxygen content, acidity and viscosity were considered, as they are crucial for the fuel's performance; however, other criteria such as LHV (lower heating value) may be further considered. Chapter 6 evaluated all six scenarios by using two distinct MCDM methods: AHP and TOPSIS – and combine the results using the aggregation method. For the AHP method, the subjective pair-wise weightings were obtained by carrying out a survey (see Appendix 2). The survey could be improved by adding other sub-criteria and consulting more experts in the field. For TOPSIS method two different pathways of achieving the weightings were considered: entropy method – where the weightings were strictly objective, and compromised weightings – where the weightings were obtained by combining entropy and pair-wise weightings. From AHP it was found that by optimising the system Scenario 6 may be a very promising option. However, by using the aggregation method between AHP method, TOPSIS with pair-wise weightings and TOPSIS with compromised weightings it was found that Scenario 2 is the most promising option. If the system is not optimised, Scenarios 1 & 4 were the more promising options in all cases (due to the lowest number of processes and the additional costs involved in each process). Further MCDM frameworks could be employed by using fuzzy logic methods – this would allow the possible ranges in sub-criteria values to be evaluated in more detail.

The contribution to the knowledge of the last objective are:
- Synthetic fuels production scenarios evaluated holistically using a combination of MCDM methods
- Esterification and esterification-ketonisation with single-stage hydrotreating identified as providing reasonable trade-offs between product quality, cost and achievable environmental gains

7.3. Assumptions and limitations of the study

This study was performed based on a number of assumptions and there are some limitations of these assumptions. For example if the plant capacity were to change, it might change the synthetic fuel capital costs. Other limitations, such as feedstock type, should be also further researched. Corn stover was chosen as an available alternative – because of previous sustainability and allocation data, but other feedstocks may influence the environmental, cost and technical results. Other possible uncertainties arise due to the assumptions made about phase separation. The percentages of light oxygenates, sugar derived and lignin derived were calculated based on corn-stover bio-oil properties and might vary for different feedstocks. Additional accuracy limitations also exist in the fixed percentage of the total capital cost allocated for the maintenance; however, other complications due to the equipment were not considered. Further limitations arise due to the criteria applied within this research; further studies may wish to focus research on methods to analyse additional criteria (not only the main ones), such as the flash point or cetane number. The latter may significantly influence the results, as in any study the inclusion or exclusion of different criteria heavily influences the final conclusions, which needs careful consideration. Another limitation is that only drop-in fuels were considered; further studies may wish to analyse the sustainability of blended biofuels (e.g. bio-oil with biodiesel or bio-butanol).

7.4. Responses to overall aim

The overall aim of this thesis was to analyse the sustainable production of synthetic fuels from waste biomass for the transport industry
It is considered that the thesis' overall aim was successfully achieved through the research outcomes. The philosophy of this thesis was to combine engineering with management principles to advance the sustainable production of synthetic fuels for the transport industry. This thesis has investigated different designs for assessing the sustainability of synthetic fuels production. The study uses separate chapters to find the best practice to produce synthetic fuels from waste biomass, assess the environmental impact, evaluate the economic feasibility and find the best design using a MCDM framework that includes AHP, TOPSIS and aggregation methods. The intended

outcomes and significance of this work is that the thesis will improve practices to reduce the environmental impacts that can occur when upgrading pyrolysis oil into synthetic fuels and ultimately promote the use of fuels, which will provide benefits over conventional fossil fuels.

The final conclusion is that even if the synthetic fuels produced from upgrading the pyrolysis oil have promising potential, the cost greatly affects the upgrading processes. Therefore, more work should be carried out to optimise the esterification process or find other alternatives for the same purpose (reduction of acidity and viscosity) and better policies that encourage biofuel production should be put in place worldwide. These measures will make synthetic fuels prices competitive to petroleum-derived fuels.

7.5. Recommendations for further work

Following the thesis achievements, some recommendations for further research can be suggested:

Recommendations for thermochemical processing:

- Further work may consider other processes: torrefaction, liquefaction, gasification or catalytic pyrolysis - however, further work may consider improving these processes yields
- Advance pyrolysis reactor design to improve the quality of the resulting bio-oil; this field has been broadly studied, but may still be improved
- Further work should be done to improve the biomass to synthetic fuel yield by advanced catalysts

Recommendations for waste biomass (bio-based) products:

- Further work on how biorefineries might integrate various bio and synthetic fuels
- Further research on bioeconomy sustainability
- Further research on biobased industries potential to reduce the dependency on fossil

Recommendations for the LCA system:

- Other LCA allocation method, such as energy allocation should be used to evaluate how this will influence the LCA results of upgraded bio-oils

- Various feedstock should be used to see how it will influence the environmental impact, but enough data on the feedstock must be available/gathered to perform the study

- GaBi professional database should be improved by adding a wider range of catalysts for biofuel production

- Future work might design and analyse a pyrolysis plant powered by renewable energy sources as solar

- Typically, phase separation has been used in the intermediate pyrolysis and was only reported once for fast pyrolysis, therefore further research in the field would be beneficial

- Further research may be using primary data from existing companies, and therefore may improve the reliability and transparency of the results

- Further work may consider more impact assessment methods (e.g. ILCD recommendations, TRACI, Eco-indicator-99, IMPACT 2000+)

Measures that will make synthetic fuels prices competitive to petroleum-derived fuels:

- Further research may use primary data for capital costs, such as raw materials, energy and taxation, including other case study countries - which will improve the results for a wider research base

- Improve the esterification process by finding a cheaper alternative to sulphuric acid catalyst which will improve the synthetic fuel yield while keeping the bio-oil to ethanol ratio near 1:1

- Find other alternatives to esterification process, for the purpose of reducing acidity and viscosity

- Synthetic fuel support policies (as financial or agricultural policies) that encourage biofuel production should be put in place worldwide

- Further cost forecasting could be carried out on the six scenarios to find out if the prices will be competitive to fossil transportation fuels in the next 30 years – or if they can be further optimised

MCDM system:

- Further work may aim to improve the survey by increasing the number of sub-criteria and the number of participants in different fields: University/Research experts, Lab experts and Industry experts

- Further research may consider more or other sub-criteria for all environmental, economic and technical impacts

- A MCDA combined fuzzy logic methodology could be further employed for finding the best technologies for producing synthetic fuels

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Appendices

Appendix 1 - Methodology example: AHP, TOPSIS with entropy and compromised weights and Aggregation methods

1. AHP Method

To simplify the understanding of the MCDM methodology, a simple example was selected and all the steps in the methodology were completed. For validation and simplification, the example was taken after the leader example - a previous AHP model (Pellizzari, 2018); but it is not identical as the alternatives criteria selection was modified.

Suppose it have to be chosen a leader for a company whose founder is about to retire. The alternatives are three candidates: Tom, John and Nick. The goal is to choose the most suitable candidate based on some criteria: experience, education, charisma and age (see Figure A1).
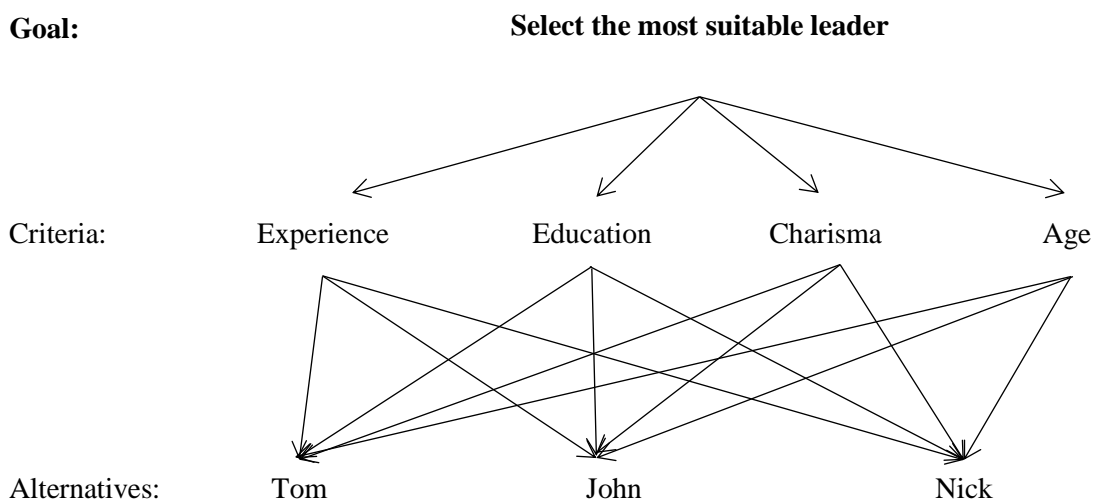

Figure A.1: AHP hierarchical framework for selecting the most suitable leader

The criteria and alternatives are first compared against each criterion by using a pairwise comparison matrix. Using factual judgment, each alternative is scored on a scale of 1 to 9 (1 – the weakest; 9 the strongest) – see Table A.1.

Table A.1: The Fundamental Scale for Pair-wise Comparisons

Intensity of importance	Definition	Explanation
1	Equal importance	Two elements contribute equally to the objective.
3	Moderate importance	Experience and judgment moderately favour one element over another.
5	Strong importance	Experience and judgment strongly favour one element over another.
7	Very strong importance	One element is favoured very strongly over another; its dominance is demonstrated in practice.
9	Extreme importance	The evidence favouring one element over another is of the highest possible order of affirmation.
Intensities of 2, 4, 6 and 8 can be used to express immediate values.		

The board decided that the experience is the most important criterion – as the founder was self-made and did not finish high school. However, the time demands imply that the new leader need to have appropriate university education. As the company project are demanding, someone with a charismatic personality is needed to motivate other staff during difficult times. Age is an appropriate factor, as the new leader need to have an appropriate path after stepping down the ladder, as the position is available for five years. By considering all the criteria against each other, the criteria pair-wise with respect of reaching the goal is presented in Table A.2a, and the pair-wise comparison matrix is presented in Table A.2b.

Table A.2: Criteria pair-wise and the resulting pair-wise comparison matrix.

a) Criteria pair-wise

Experience	4	Education	1
Experience	3	Charisma	1
Experience	7	Age	1
Education	1	Charisma	3
Education	3	Age	1
Age	1	Charisma	5

b) Pair-wise comparison matrix

Criteria	Experience	Education	Charisma	Age
Experience	1	4	3	7
Education	1/4	1	1/3	3
Charisma	1/3	3	1	5
Age	1/7	1/3	1/5	1
Total	*1.73*	*8.33*	*4.53*	*16*

The pair-wise comparison matrix was obtained by pairing the criteria. The matrix is normalized by dividing each cell by its corresponding column total. The average or each row of the normalized matrix provides the priority vector of the criteria. The normalized matrix and the weighting vector are presented in Table A.3:

Table A.3: Normalized matrix and the weighting vector of the criteria

Criteria	Experience	Education	Charisma	Age	*Weighting Vector*
Experience	0.58	0.48	0.66	0.44	*0.54*
Education	0.14	0.12	0.07	0.19	*0.13*
Charisma	0.19	0.36	0.22	0.31	*0.27*
Age	0.08	0.04	0.04	0.06	*0.06*

The alternatives are assumed to be three candidates: Tom, John and Nick and their characteristics are presented in Table A.4:

Table A.4: Candidates characteristics

Alternatives/Criteria	Tom	John	Nick
Age	50	60	30
Experience	10 years in the company 16 years in other industry Currently VP Sales & Customer services	30 years in the company 8 years in other company, same industry Currently Executive VP	4 years in the company 5 years in other industry Currently VP Finance
Education	BS College 26 year ago, online MBA last year	BA and MA University, 39 years ago	BS University 10 year ago, MBA 5 years ago
Charisma	An active inspirational leader	A bit reserved – leads by example	Leads quietly by its office

Following the board deliberation on the criteria of each alternative above it was decided to score each leader against the criteria. The scoring is shown in the table below:

Table A.5: Scoring of each leader against each criteria

Criteria/Alternatives	Experience	Education	Charisma	Age
Tom	3	5	9	5
John	9	1	3	9
Nick	1	7	1	1

Based on the scorings above were constructed the pair-wise matrix and calculated the priority vectors of each criterion, the same way it was done in alternative case (see Tables A.2 & A.3). The weighting vector of the criteria and the priority vector of each criterion against the alternatives were calculated and are shown in Figure A.2.

Goal: **Select the most suitable leader**
[1]

Criteria:	Experience [0.54]	Education [0.13]	Charisma [0.27]	Age [0.06]
Alternatives:	Tom [0.23]	Tom [0.38]	Tom [0.69]	Tom [0.33]
	John [0.69]	John [0.08]	John [0.23]	John [0.60]
	Nick [0.08]	Nick [0.54]	Nick [0.08]	Nick [0.07]
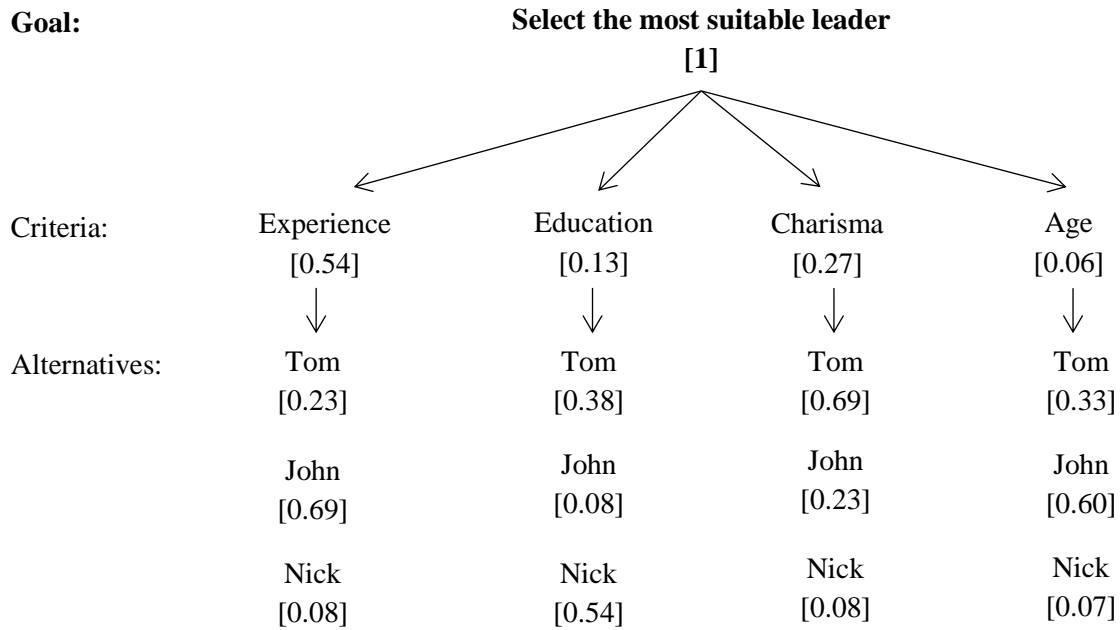
Figure A.2: Updated hierarchy tree showing the calculated priorities

The preference of each leader is calculate by multiplying each alternative's priority by the corresponding criterion's weighting. The final ranking can be expressed as a percentage and is given in the Figure A.3.
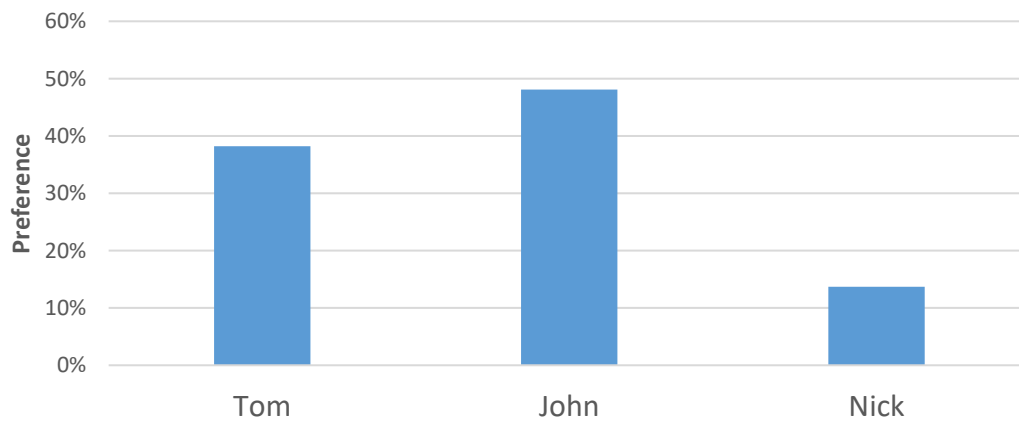
	Tom	John	Nick
Experience	0.125	0.374	0.042
Education	0.051	0.10	0.071
Charisma	0.188	0.063	0.021
Age	0.019	0.034	0.004
Total	38.22%	48.08%	13.70%

Figure A.3: The final rankings using the AHP method

By performing the AHP method it was found that John is the preferred candidate for the leadership position with 48.08%, followed by Tom and the least preferred one is Nick.

The consistency check was performed to find the reliability of the model, and the possible mistakes. λ_{max} (eigenvalue) was found to be 4.12 resulting in a consistency index of approximately 0.04. The random consistency index for four criteria is 0.9 (Alonso and Lamata, 2006) and the consistency ratio was found to be 0.044% or 4.4%, which is smaller than 10%, resulting the criteria have an acceptable consistency and the model is valid.

2. TOPSIS Method

Step 1: Construct the decision matrix and determine the criteria weights

Scoring of each leader against each criteria matrix (Table A.4) is normalised using more is better method. The weightings were calculated by using the entropy method and compromise (combined) method. The resulted matrix and the weightings are presented in Table A.6:

Table A.6: Normalised matrix using more is better method and the weightings

Normalised values	Experience	Education	Charisma	Age
Tom	0.25	0.67	1	0,5
John	1	0	0.25	1
Nick	0	1	0	0
Entropy Weightings	0.29	0.20	0.29	0.22
Compromised Weightings	0.57	0.10	0.29	0.05

Step 2: Calculate the normalized decision matrix

The data from Table A.4 was normalised, resulting the normalised decision matrix, see Table A.7. This normalisation must be performed especially when each criterion is measured in different units.

Table A.7: Normalised decision matrix

Normalised matrix	Experience	Education	Charisma	Age
Tom	0.314	0.577	0.943	0.483
John	0.943	0.115	0.314	0.870
Nick	0.105	0.808	0.105	0.097

Step 3: Calculate the weighted normalised decision matrix

The weighted normalized matrix was calculated by multiplying the columns of the normalized decision matrix by the associated weights. As the entropy (Ent.) weightings values and the compromised (Com.) weightings values are different, result two different matrixes, as shown in Table A.8.

Table A.8: Weighted normalised matrix

Weighted norm. matrix	Experience		Education		Charisma		Age	
Method	Ent.	Com.	Ent.	Com.	Ent.	Com.	Ent.	Com.
Tom	0.09	0.179	0.118	0.057	0271	0.27	0.107	0.023
John	0.271	0.536	0.024	0.011	0.09	0.09	0.193	0.041
Nick	0.03	0.06	0.165	0.08	0.03	0.03	0.021	0.005

Step 4: Determine the best and the worst alternatives

The positive ideal alternative is the best alternative and maximizes the benefit criteria and minimizes the cost criteria (see Table A.9).

Table A.9: Positive ideal alternative – best alternative

Positive ideal alt.	Experience		Education		Charisma		Age	
Method	Ent.	Com.	Ent.	Com.	Ent.	Com.	Ent.	Com.
Tom	0.271	0.536	0.165	0.08	0.271	0.27	0.193	0.041
John	0.271	0.536	0.165	0.08	0.271	0.27	0.193	0.041
Nick	0.271	0.536	0.165	0.08	0.271	0.27	0.193	0.041

The negative ideal alternative is the worst alternative and maximizes the cost criteria and minimizes the benefit criteria (see Table A.10).

Table A.10: Negative ideal alternative – worst alternative

Negative ideal alt.	Experience		Education		Charisma		Age	
Method	Ent.	Com.	Ent.	Com.	Ent.	Com.	Ent.	Com.
Tom	0.03	0.06	0.024	0.011	0.03	0.03	0.021	0.005
John	0.03	0.06	0.024	0.011	0.03	0.03	0.021	0.005
Nick	0.03	0.06	0.024	0.011	0.03	0.03	0.021	0.005

Step 5: Measure distance from the positive ideal solution and the negative ideal solution

The distance from the positive ideal solution was calculated using the Weighted normalised matrix and the Positive ideal alternative matrix and is the distance from of the target alternative to the best state. The distance from the negative ideal solution was calculated using the Weighted normalised matrix and the Negative ideal alternative matrix and is the distance from of the target alternative to the worst state. The distance from positive and negative ideal solutions are shown in Table below.

Table A.11: The distance from Positive and Negative ideal solutions

Alternatives	Distance from the positive ideal solution		Distance from the negative ideal solution	
Method	Ent.	Com.	Ent.	Com.
Tom	0.21	0.36	0.28	0.27
John	0.23	0.19	0.30	0.48
Nick	0.38	0.54	0.14	0.07

Step 6: Calculate the similarity to the ideal condition

The similarity to the ideal condition is calculated as a function of the distance from Positive ideal solution and the distance from Negative ideal solution (see Table A.12).

Table A.12: The similarity to the ideal condition

Alternatives	The similarity to the ideal condition	
Method	Ent.	Com.
Tom	0.58	0.43
John	0.57	0.71
Nick	0.27	0.11

Step 7: Rank the preference order

The higher the closeness to 1 means a higher rank; the alternatives rank are shown in the table below:

Table A.13: Alternatives rank and percentages for TOPSIS with entropy and compromised weightings

Alternatives	Preference ranking	
Method	Ent.	Com.
Tom	1 (41%)	2 (34%)
John	2 (40%)	1 (57%)
Nick	3 (19%)	3 (9%)

Aggregation method

The ranking of all three methods used: AHP, TOPSIS with entropy weightings and TOSIS with compromised weightings are shown in the table below.

Table A.14: Alternatives rank for AHP, TOPSIS with entropy and compromised weightings

Alternatives	Preference ranking		
Method	AHP	TOPSIS with Ent.	TOPSIS with Com.
Tom	2	1	2
John	1	2	1
Nick	3	3	3

Two different voting methods: Borda and Coperland were used to obtain the final ranking from all the previous methods. The final ranking and the percentages from both methods are very similar and are shown in the Table A.15:

Table A.15: Final rankings using Borda and Coperland

Alternatives	Preference ranking	
Method	Ent.	Com.
Tom	2 (36%)	2 (37%)
John	1 (39%)	1 (40%)
Nick	3 (25%)	3 (23%)

By using both aggregation methods resulted that John is the preferred candidate for the leadership position with 39-40%, followed by Tom with 36-37%; and the least preferred candidate is Nick with only 23-25%.

Appendix 2 - The survey used for AHP method with average values, obtained from experts' opinion.

The survey was sent to 25 experts in the field. It targeted experts that work in academic, laboratory and industrial domains. The participation rate was only 12%. However, because the three experts covered all the desired areas it was decided that the survey result was reliable.

SURVEY

This survey aims to determine which criteria (clusters) have greater weight, for analysing biofuels sustainability. The study generally aims to analyse the sustainable production of synthetic fuels from biomass for the transport industry. The questions should be completed based on your expertise and do not require any technical data. Please complete pages 3&4.

Environmental impacts:
- ❖ GWP – global worming potential is a relative measure of how much heat greenhouse gas traps in the atmosphere. GWP unit is kg CO_2 equivalent.
- ❖ AP – acidification potential is a meter of the disposition of a unit of the mass of a component i to release H^+ protones, expressed in terms of the H^+ potential of the reference substance SO_2. Acidification - acid gases that are released into the air or resulting from the reaction of non-acid components of the emissions are taken up by atmospheric precipitations and the falling "acid rain" forms an acid input which is absorbed by plants, soil and surface waters leading to leaf damage and superacidity of the soil, which in turn affects the solubility and hence availability of plant nutrients and trace elements plants can take in.
- ❖ EP – eutrophication potential is based on the work of Heijungs, and is expressed using the reference unit, kg PO_4 equivalents. Eutrophication - can be classified as the over-enrichment of water courses. Its occurrence can lead to damage of ecosystems, increasing mortality of aquatic fauna and flora and to loss of species dependent on low-nutrient environments. Emissions of ammonia, nitrates, nitrogen oxides and phosphorous to air or water all have an impact on eutrophication.

Economic impacts:
- ❖ Capital
- ❖ Operational costs
- ❖ IRR (internal rate of return) based on the minimum selling price

Technical impacts:
- ❖ Oxygen content
- ❖ Viscosity
- ❖ Acidity

Social impacts:
- ❖ Community acceptance
- ❖ Policy
- ❖ Local impact

Questionnaire:

You are required to use the following scale for each main criterion (cluster) according to its degree of importance to another criterion.

Intensity of importance	Definition	Explanation
1	Equal importance (less important)	Two elements contribute equally to the objective.
3	Moderate more importance (of one over the other)	Experience and judgement moderately favour one element over another.
5	Strong more importance	Experience and judgement strongly favour one element over another.
7	Very strong more importance	One element is favoured very strongly over another; its dominance is demonstrated in practice.
9	Extreme more importance (most important)	The evidence favouring one element over another is of the highest possible order of affirmation.
Intensities of 2, 4, 6 and 8 can be used to express immediate values. Intensities of 1.1, 1.2, 1.3, etc. can be used for elements that are very close in importance.		

Example:

Which impact is more important...?

Criteria	Impact 1	Impact 2	Impact 3	Impact 4	Other - optional
Importance	1	3	9	7	[3]

Q1. Which impact is more important for producing sustainable transportation synthetic fuels?

Clusters	Environmental	Economic	Technical	Other
Importance	5	7	7	-

If other, please give details below:

Q2. Which environmental impact is more important for producing sustainable transportation synthetic fuels?

Criteria	GWP	AP	EP	Other
Importance	4.33	4.33	4.33	-

If other, please give details below:

All impacts are equally important - a fuel which meets all the needs but has an unacceptable impact somewhere is not sustainable

Q3. Which cost impact is more important for producing sustainable transportation synthetic fuels?

Criteria	Capital Cost	Operational Cost	IRR (or the selling price)	Other
Importance	6.33	5.33	6.66	

If other, please give details below:

Other – taxation [9]

Q4. Which technical impact is more important for producing sustainable transportation synthetic fuels?

Criteria	Oxygen content	Viscosity	Acidity	Other
Importance	6.66	5.33	5.33	3

If other, please give details below:

Quality and standards

Additional information

Is there any additional information to help in this study?

Viable bio-fuel production must be within a zero-waste bio-refinery also producing higher value chemicals and materials….like a petroleum refinery!
Need to ensure the right biomass feed…not food competitive in any way and not requiring many additional costs like transportation of biomass.

In case of any query of clarification required pertaining this questionnaire, please contact me: k1250144@kingston.ac.uk

Thank you very much for your time and participation!

Appendix 3 - Publications

The published work outlined below will be attached further to this thesis:

- Bioresource Technology Journal:

  D.N. Vienescu, J. Wang, A. Le-Gresley, J.D. Nixon: A life cycle assessment of options for producing synthetic fuel via pyrolysis. Bioresource Technology 249 (2018) 626-634, (IF 6.1/Q1)

- Conference proceeding paper:

  D.N. Vienescu, J. Wang, A. Le-Gresley, J.D. Nixon: The impact of using hydrogen to upgrade pyrolysis oils, 4th International Conference on Energy, Environment and Sustainable Development, EESD 2016, MUET University, Pakistan