Evaluation of the energy efficiency of liquid biofuel synthesis using energy quality metrics

by

Gabriela Steenekamp
17131066

Supervised by
Dr Ryan Merckel

Dissertation submitted in partial fulfilment of the requirements for the degree

Master of Engineering (Chemical Engineering)

Department of Chemical Engineering
Faculty of Engineering, the Built Environment and Information Technology
University of Pretoria
South Africa

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

August 2024

Ethics statement

The author, whose name appears on the title page of this dissertation, has obtained the required research ethics approval/exemption for the research described in this work.

The author declares that they have observed the ethical standards in terms of the University of Pretoria's Code of ethics for scholarly activities.

Gabriela Steenekamp
Date: 29 July 2024

Abstract

Biofuel production is a rapidly growing industry that aims to eventually replace non-renewable fuels. A consequence of biofuel synthesis is the abundant production of waste biomass, or lignocellulosic material. The lignocellulose may be utilised for biofuel production in the second generation process, or converted to process energy.

The efficacy of industrial-scale biofuel processes are conventionally measured in life-cycle assessment studies using energy balances in the form of the fossil energy ratio (FER) and the net energy ratio (NER). The application of these metrics, however, have considerable drawbacks. It was shown in this study that these traditional metrics provide reversed indications of "renewability" when cogeneration of biomass is considered.

Process models were developed from literature to evaluate the production of bioethanol from sugarcane and biodiesel from soybean from a process energy-efficiency perspective. The utilisation of the waste- and by-products was assessed in various process scenarios. A set of grounded and robust metrics were employed to evaluate the efficiency of the processes, namely, the change in energy quality and the change in energy yield. The change in energy quality evaluates whether there has been an increase in the energy density from the feedstock to the product. The change in energy yield, on the other hand, quantifies the amount of energy transferred from the feedstock to the biofuel, where the energy consumption of the process is taken into account.

The change in energy quality for bioethanol and biodiesel showed a 63 % and 107 % increase compared to the respective parent crops. Even with the improvement in energy density, the change in energy yield achieved is only 10 %–27 % for biodiesel and 28 %–36 % for bioethanol. Compared to the ideal route of upgradation possible for soybean and sugarcane, the maximum energy recovered from soybeans is less than 28 % of the ideal case, and from sugarcane, it is less than 46 %.

For the soybean-biodiesel configurations explored, the change in energy yield increases by up to 161 % when the waste- and by-product streams are utilised for process energy. For the sugarcane-to-bioethanol process, the valorisation of the lignocelluose to bioethanol in the second generation process was also explored. The second generation process contributes marginally to the change in energy yield, where only a 3 % increase is seen compared to traditional first generation processes with cogeneration. From an energy perspective, the benefits of second generation bioethanol cannot be justified with regard to the additional infrastructure.

The energy recovery of both processes suffer because the feedstocks, the sugarcane crop and the soybean crop, are predominantly composed of lignocellulose—straw, meals/hulls, or bagasse. The extractible intermediate feedstocks, saccharides from sugarcane and oil from soybeans, are only a fraction of the entire biomass. As a result, there are pronounced energy losses from the lignocelullosic by-products even when used for process energy generation or second generation biofuel production.

This sentiment is also seen when comparing the end-use of the fuel and the feedstock: the biomass-to-fuel-to-engine cycle yields a lower change in energy yield compared to converting the biomass directly to electricity. There are pronounced inefficiencies in the naturally guided synthesis pathways that are difficult to overcome.

Focus should be placed on utilising suitable feedstocks for biofuel production and industrialising fuel production pathways that maximise energy recovery from the entire parent biomass.

Keywords: Bioethanol; biodiesel; lignocellulose; energy metrics; energy yield; energy quality; first generation; second generation

Acknowledgements

I would like to extend my deepest gratitude to my parents and brother. You have maintained unconditional support throughout my life's goals, whether turbulent or fruitful. I owe you everything I have achieved and have yet to achieve.

To my friends and partner, I am the person I am today because of the calibre of people that surround me. Thank you for your encouragement and your loving influence.

To Mrs Elizbé du Toit, I admire your eagerness to advise and assist whenever called upon. Thank you for your insights and interest in my research.

To my supervisor, Dr Ryan Merckel. You have provided me with a platform to explore the foundations of your research. Thank you for your supervision, your support, and the conveyance of your knowledge. My perspective on engineering has been enriched by you.

> *We don't accomplish anything in this world alone... and whatever happens is the result of the whole tapestry of one's life and all the weavings of individual threads from one to another that creates something.*
>
> Sandra Day O'Connor

Contents

List of Figures

List of Tables

Nomenclature

$\Delta \mathrm{H}_{\mathrm{vap}}$	Heat of vaporisation of water	MJ kg^{-1}
$\Delta E_{\mathrm{cons.}}$	Energy consumed	MJ
ΔE_{f}	Energy of feedstock	MJ
ΔE_{p}	Energy of products	MJ
ΔE_{Q}	Change in energy quality	%
ΔE_{η}	Energy yield	%
ΔH	Change in enthalpy	MJ kg^{-1}
$\Delta_c h^{\circ}\|_{\mathrm{HHV,f}}$	Higher heating value of feedstock (daf)	MJ kg^{-1}
$\Delta_c h^{\circ}\|_{\mathrm{HHV,p}}$	Higher heating value of products (daf)	MJ kg^{-1}
$\dot{Q}$	Heat transfer	MJ h^{-1}
η	Mass yield	%
η_{boiler}	Boiler efficiency	%
$\eta_{\mathrm{generator}}$	Electrical generator efficiency	%
η_{pump}	Isentropic pump efficiency	%
η_{turbine}	Isentropic turbine efficiency	%
γ	Heat of combustion constant	MJ $\mathrm{kg}_{\mathrm{O}_2}^{-1}$
ρ	Density	kg m^{3}
C	Heat capacity rate	MJ K^{-1}
$E_{\mathrm{elec.\ cons.}}$	Electricity consumed for biofuel production	MJ h^{-1}
E_{fossil}	Fossil fuel energy consumed	MJ h^{-1}
$E_{\mathrm{generated}}$	Total electricity generated in cogeneration	MJ h^{-1}
E_{surplus}	Surplus electricity generated after cogeneration	MJ h^{-1}

h	Specific enthalpy	MJ kg^{-1}
M	Molar mass	kg kmol^{-1}
m_{biomass}	Mass of biomass used for process energy	kg h^{-1}
n_ν	Number of moles	kmol
Q_{boiler}	Boiler heat requirement	MJ kg^{-1}
s	Specific entropy	MJ kg^{-1}
W	Specific work	MJ kg^{-1}
m_{f}	Mass of feedstock (daf)	kg
m_{O_2}	Mass of oxygen consumed during combustion	kg
m_{p}	Mass of products (daf)	kg
AR	As received basis	-
daf	Dry and ash free basis	-
FER	Fossil energy ratio	-
HHV	Higher heating value	MJ kg^{-1}
LCA	Life-cycle assessment	-
LHV	Lower heating value	MJ kg^{-1}
LM	Lignocellulosic material	-
LPG	Liquid pretroleum gas	-
NER	Net energy ratio	-
SBD	Soybean biodiesel	-
SBE	Sugarcane bioethanol	-
t_{beans}	Ton of soybeans sent to biodiesel processing (AR basis)	-
t_{cane}	Ton of sugarcane sent to bioethanol processing (AR basis)	-
TTW	Tank to wheel	-

Chapter 1: Introduction

1.1 Background

The use of petroleum, diesel, and other liquid fuels in the transportation sector are responsible for a large portion of the global greenhouse gas emissions (Ayodele, Alsaffar & Mustapa, 2020). Distress over depleting fossil fuel reserves and accelerated climate change has led to a growing imperative to transition towards renewable sources for transportation energy. Biofuels are universally appraised as a solution to this motive (Larson, 2008; Verma & Sharma, 2016).

Bioethanol, followed by biodiesel, hold the largest demand in the biofuel production market globally. This is largely due to advanced government policies that drive bioethanol blends with petroleum and the use of biodiesel directly in automobile engines (Niphadkar, Bagade & Ahmed, 2018; Meira *et al*, 2015). In 2023, the reported annual production of bioethanol was 112 billion litres (Renewable Fuels Association, 2023) and for biodiesel, 86.4 billion litres (Statista, 2023). The International Energy Agency (2023) reports that the biofuel demand is projected to increase by 28 billion litres from 2023 to 2028, where bioethanol and biodiesel make up about 66 % of the expected growth in production.

Historically, biofuels have been produced from food-based feedstocks; this is generally categorised as first generation (1G) biofuels (Meira *et al*, 2015). The technology and markets for 1G bioethanol and biodiesel are very mature (Niphadkar *et al*, 2018) and the processes has been industrialised for more than two decades (Ayodele *et al*, 2020). For this study, the most widely used feedstocks are considered: sugarcane for bioethanol and soybeans for biodiesel (Souza, Seabra & Nogueira, 2018; Borugadda & Goud, 2012; Kim & Dale, 2004; Duque *et al*, 2021).

The ever increasing demand and production of first generation biofuels, however, is not without consequence: utilising food crops for fuel threatens global food security (Naik *et al*, 2010; Bezerra & Ragauskas, 2016; Fulton *et al*, 2015); the high water-demand for crop cultivation poses environmental and sustainability challenges (Borrion, McManus & Hammond, 2012; Rodriguez *et al*, 2018), and the environmental impact of land-use change due to feedstock agriculture has not been fully quantified (Ayodele *et al*, 2020). To address these challenges, there has been a heightened interest in second generation (2G) biofuel production which employs non-edible feedstocks. Significantly, research and development has been focused on utilising crop residues and lignocellulosic biomass for the production of biofuels.

Crop residues, also known as straw or trash, are the lignocellulosic by-products that remain after the crop is harvested (Lal, 2005). Globally, about 200 billion tonnes of biomass trash is produced annually making it an extremely inexpensive and abundant resource for bioenergy conversion (Kamusoko *et al*, 2021; Loh *et al*, 2013; Hernández-Salas *et al*, 2009). Traditionally, straw has been buried in the soil for fertilisation (Kamusoko *et al*, 2021). However, the optimal fraction of straw left on the fields for soil conservation is less than what is produced (Almeida & Colombo, 2021). As a result, excess straw has been conventionally considered as a waste product that has been sent to land-filling or incinerated on the fields to prepare the area for the following season which poses environmental issues (Leal *et al*, 2013; Cabrera *et al*, 2015; Kamusoko *et al*, 2021). The straw remains a largely unexploited resource for bioenergy in most facilities. This has been mainly due to the underdeveloped infrastructure for storage and transport of field straw to the processing operations (Leal *et al*, 2013; Pereira *et al*, 2015).

In contemporary facilities, sugarcane bagasse[1] is used as a fuel-source for the generation of process steam and electricity (Leal *et al*, 2013; Pippo *et al*, 2011; Kumar, Kumar, Singh, *et al*, 2021)—this is known as cogeneration. The energy recovered from the sugarcane by-products and residues allows production facilities to achieve energy self-sufficiency and to sell surplus electricity to the grid (Dias, Modesto, *et al*, 2011; Kanoglu & Dincer, 2009; Dias, Junqueira, Cavalett, Cunha, Jesus, Mantelatto, *et al*, 2013).

Although cogeneration is an established practice, the production of second generation fuels from biomass residues has received growing interest in the past decades (Gonzalez *et al*, 2023). The upgradation of lignocellulosic material to fuel promises to combat the adverse impacts of 1G production (Duque *et al*, 2021). The body of literature concerned with valorising lignocellulosic biomass involves thermochemical conversion using liquefaction (Tian *et al*, 2020), gasification (Wang *et al*, 2020; Cabrera *et al*, 2015), cabonization (Wang *et al*, 2020), pyrolysis (Branca, Di Blasi & Galgano, 2017) and more. However, these technologies are not yet mature and have their respective challenges. The most advanced method of biofuel production from lignocellulosic waste is the production of bioethanol through hydrolysis. According to Karp *et al* (2021), there are two industrial-scale 2G bioethanol plants in Brazil, where sugarcane bagasse and straw are valorised to bioethanol using steam explosion and enzymatic hydrolysis.

Clearly, there is a shift in interest in the utilisation of these residues, from waste disposal, to cogeneration, and to biofuel production. The desirability of the feedstock for

---

[1] Sugarcane bagasse is the fibrous material that remains after the sugar-rich juices have been extracted from the sugarcane stalk

cogeneration *vs.* biofuel production is still under scrutiny where comparisons are being drawn based on techno-economic studies, life-cycle assessment criteria, or other metrics (Hiloidhari *et al*, 2018; Persson *et al*, 2009). Grounded metrics are essential to evaluate the most efficacious use of these residues, and biofuel conversion processes as a whole.

Life-cycle assessment (LCA) studies employ the fossil energy ratio (FER) and the net energy ratio (NER) to determine the energy recovery and renewability of biofuel production processes. Life-cycle assessment studies have been generally accepted as the standard to determine the efficacy of renewable processes, specifically from an environmental and sustainability point of view. However, the application of the fossil energy ratio and the net energy ratio in LCAs are executed using wide system boundaries that make the results difficult to reproduce, and allocation methods are applied which undermine the energy evaluation of process systems. The FER and NER may be sensible to determine process renewability, but not necessarily the energy utilisation of the feedstock to the biofuel. In order to assess the energy recovery of biofuel upgradation processes, grounded and easily applied methods are required.

In kind, Merckel, Labuschagne & Heydenrych (2020) have demonstrated the strong correlation of the higher heating value on the mass of consumable oxygen of the fuel. On this basis, the authors present easily applied energy metrics to assess biomass-to-biofuel conversion processes, namely, the change in energy quality, ΔE_{Q}, and the change in energy yield, ΔE_{η}.

1.2 Problem statement

This study aims to evaluate the sugarcane-derived bioethanol and soybean-derived biodiesel production processes from a process energy-efficiency perspective, specifically by applying the change in energy quality and the change in energy yield. Only industrialised processing methods are considered to present a relevant assessment. The parent biomass (the sugarcane crop and the soybean crop) are taken as the direct energy input into the respective processes. The entire crop is accounted for as the reference state to evaluate the energy efficacy of utilising food-crops for fuel synthesis. There are existing sociological and environmental challenges of first generation (1G) biofuel production; therefore, the use of food crops for 1G biofuels should also be assessed through the lens of energy efficiency.

The sugarcane-bioethanol and soybean-biodiesel conversion processes are modelled and the mass and energy balances are determined using literature process parameters. The use of the crop residues from sugarcane and soybean processing are also considered in the models for bioenergy conversion. In this way, the contribution of the residues to the overall-system energy-recovery may be determined and compared. For the soybean-biodiesel process, the by-products are evaluated for the production of process steam and electricity in cogeneration. The upgradation of the by-products for 2G biodiesel is not modelled as 2G biodiesel production is not yet a mature technology. For the sugarcane-bioethanol process, however, the by-products are evaluated in terms of their use for cogeneration and for 2G bioethanol production.

1.3 Objectives

This study aims to accomplish the following:

- Develop reliable process models for 1) 1G bioethanol production 2) 1G biodiesel production, 3) cogeneration of the by-products, and 4) 2G bioethanol production from lignocellulose.
- Evaluate various configurations of the biomass-to-biofuel models where the recovery of the by- and co-products are analysed. The analyses of different process scenarios is intended to investigate the energy loss-mitigation possible from lignocellulose recovery during cogeneration *vs.* second generation biofuel production.
- Determine the ideal upgradation routes of the feedstocks to the biofuels as a point of comparison. The theoretical maximum is intended to provide insights into the applicability of the feedstock and the inefficiencies of real biofuel production processes.
- Apply the energy metrics, ΔE_{Q} and ΔE_{η}, for each process scenario on an overall basis. The final achievable energy metrics may then be compared to determine the optimal configurations.
- Apply the energy metrics, ΔE_{Q} and ΔE_{η}, to different process scenarios on a cumulative per-unit-operation basis. The contribution of each unit operation may then be evaluated.
- Analyse the end-use of the biofuel in an internal combustion engine and the direct conversion of biomass to electricity. The comparison is intended to evaluate the energy recoverable from the direct use of the parent biomass for electricity *vs.* the energy recovered from biomass-to-biofuel-to-mechanical energy.

- Apply the fossil energy ratio and the net energy ratio to different biofuel production process scenarios. The applicability of the change in energy quality and the change in energy yield may then be compared to these conventional metrics.

1.4 Research questions

This dissertation aims to answer the following questions:

- How suitable is sugarcane for bioethanol production and soybean for biodiesel production?
- What is the optimal use of the by- and co-products of the biomass?
- Are the fossil energy ratio and the net energy ratio suitable metrics to evaluate the efficiency of biomass upgradation processes?
- Where should the focus be placed in the field of research of biofuels?

1.5 Scope and limitations

This study has developed specific models for bioethanol and biodiesel production from sugarcane and soybean respectively. The models are largely based on available literature, where discretion is employed to validate the model parameters. The model development is therefore specific to these feedstocks. To apply a holistic and overarching criticism on biofuel processes, all available and feasible feedstocks should be evaluated.

Importantly, this study is limited to current, industrially employed methods of biofuel production. The study has not taken into account promising biofuel synthesis pathways that are not yet mature.

Although this dissertation discusses life-cycle analyses and the energy metrics applied in these studies, this dissertation is not, in fact, a life-cycle assessment. The system boundary of the biofuel production models are defined specifically to consider direct material and energy inputs into the process. The system boundary is intended to reflect the boundary of the production process. The applicability of the energy metrics to any local process can therefore be demonstrated. In contrast, life-cycle assessments extend the system boundary to consider the life-cycle energy of every material stream and energy stream. This study is therefore limited in its capacity to extend its results and conclusions to the holistic life-cycle of biomass upgradation.

1.6 Dissertation structure

The structure of this dissertation is outlined in Figure 1.1 below:

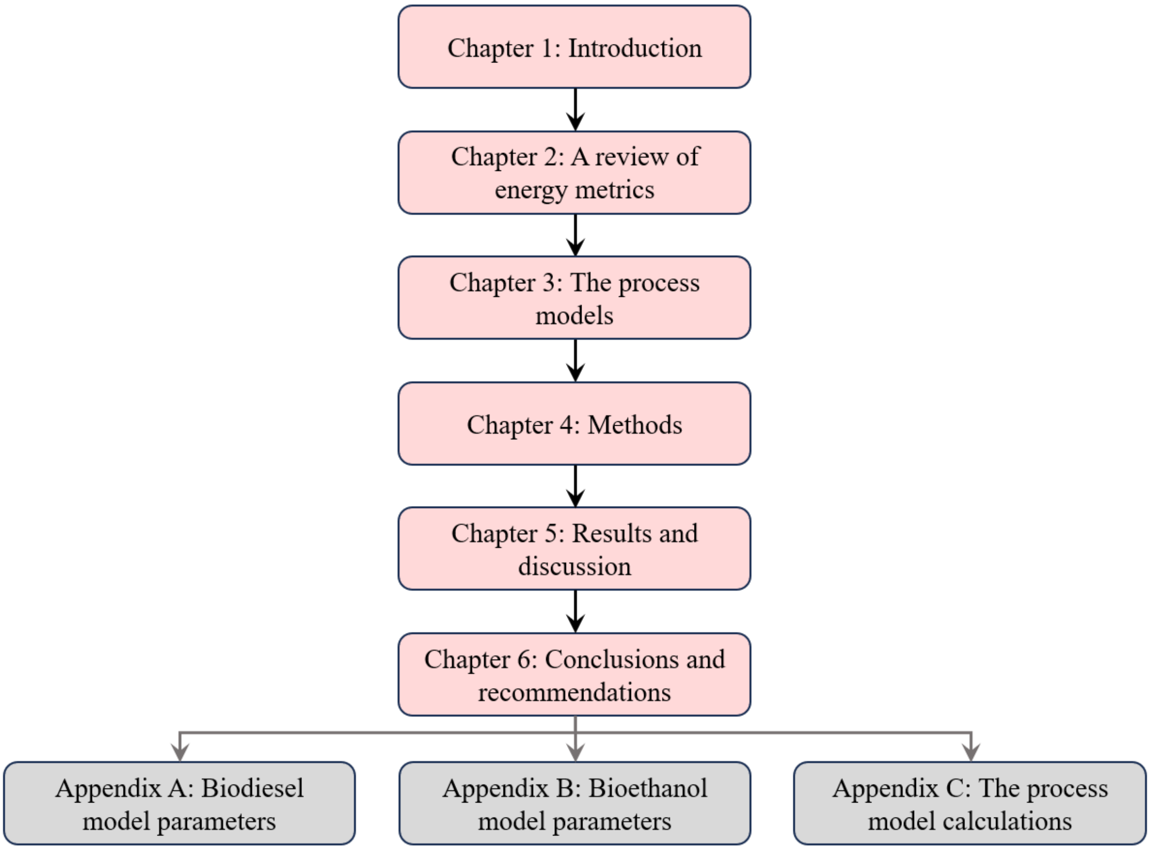


Figure 1.1: The structure of the dissertation.

Chapter 1 is the introduction of the study's objectives and scope.

Chapter 2 provides a review of current methods of biofuel energy-assessments. Here, the methods employed by life-cycle assessments are discussed and the shortcomings outlined. The supporting research and the definitions of the change in energy quality and the change in energy yield are elucidated.

Chapter 3 presents the process models for soybean-biodiesel, sugarcane-bioethanol, and cogeneration. Literature is reviewed and discussed to define the model parameters of each process.

Chapter 4 describes the methods used to evaluate the energy metrics of the process models. The energy metrics are discussed and the scenarios for the bioethanol and biodiesel processes are defined.

Chapter 5 presents and discusses the results for each scenario for each biofuel production model.

The conclusions and recommendations of this study are contained in Chapter 6.

The process parameters used to model the soybean-biodiesel and sugarcane-bioethanol process are provided in Appendix A and Appendix B respectively.

The raw models may be accessed through a link attached in Appendix C. The process models were developed in Microsoft Excel (Microsoft Corporation, 2024) and Python (Van Rossum & Drake, 2009).

Chapter 2: A review of energy metrics

2.1 Life-cycle assessments and the shortcomings

Life-cycle assessments (LCAs) have been regarded as the standard for evaluating the sustainability and energy efficiency for biofuel systems and have been widely used by industry and governments for the development of biofuel policies (Raugei *et al*, 2014; Liska & Cassman, 2008). These studies evaluate the "cradle-to-grade", or the "life-cycle", of the biomass (Emiola-Sadiq, Zhang & Dalai, 2021). A cradle-to-grave approach assesses the biomass cycle at the point of seed, to cultivation, to biofuel conversion and refining, and to its end-use. LCAs take inventory of all material and energy fluxes. The environmental impact of the process is then evaluated relative to the sustainability and energy-demand of the process-inputs.

Standards such as ISO 14040:2006 define the goals, scope, and principles of life-cycle assessments and their interpretation (Technical Committee ISO/TC 207, 2006). Although guidelines do exist, results based on LCA methods vary widely due to differences in 1) data collection, 2) the scope and system boundary, 3) the application of energy balances and metrics, and other factors (Czyrnek-Delêtre, Smyth & Murphy, 2017).

The following sub-headings are the main aspects that result in variability among LCA studies in terms of the energy assessments. Although life-cycle assessment studies are largely intended for renewability and sustainability measures, the following discussion focuses on the measurement of energy-efficiency, as is the objective of this dissertation.

2.1.1 The system boundary of life-cycle assessments

There is no single system boundary that is universally employed in LCA studies. The system boundary depends on how expansive the inputs into the process are, for example, whether the energy cost is considered for manufacturing agricultural and processing equipment, labour, building infrastructure, and so on (Pradhan, Shrestha, Van Gerpen, *et al*, 2008).

Among almost all LCAs, however, the following inputs are considered:

- All energy inputs into the process—these are usually in the form of fossil fuels (*e.g.*, diesel, natural gas, and coal), electricity, steam, and others.
- Energy associated with the material inputs (*e.g.*, fertilisers, pesticides, and processing chemicals).
- Fuel consumption to transport the feedstock, intermediate products, and the biofuel between the farms, refineries, and filling stations.

An example system boundary is shown in Figure 2.2. The outputs that are considered for the energy balance is the energy contained in the biofuel and any surplus electricity produced during cogeneration.

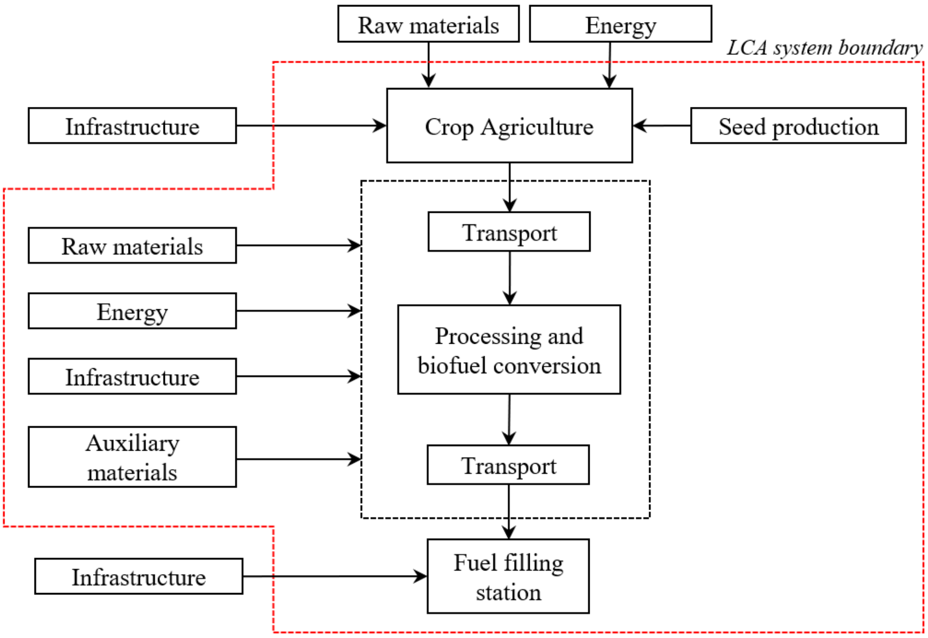


Figure 2.1: Example of an LCA system boundary. *The figure was adapted from Morais, Martins & Mata (2010) and Pradhan, Shrestha, Van Gerpen,* et al *(2008).*

2.1.2 Calorific value *vs.* life-cycle energy

Studies disagree on the assignment of energy values to the fuel and material inputs into the process. The calorific value of a fuel is a straight forward consideration for evaluating energy consumption. For some LCAs, the "life-cycle energy equivalent" is used to determine the energy consumption associated for all inputs into the process (Pradhan, Shrestha, Van Gerpen, *et al*, 2008). This "energy equivalence" essentially considers the life-cycle of the input. For example, natural gas may have a calorific value of 47 MJ kg^{-1}, however, to obtain the natural gas in its usable form for use at the processing plant, energy was consumed to extract and refine the fuel. The life-cycle energy accounts for this, where it is always higher than the input's calorific value. The life-cycle energy equivalent is also assigned to material inputs that do not have an inherent calorific value, such as water and fertilisers. Some examples of the calorific value and the life-cycle energy equivalent for energy and material inputs are shown in Table 2.1:

Table 2.1: The calorific value *vs.* the life-cycle energy equivalent used by some literature studies to conduct an LCA energy balance for soybean-derived biodiesel.

Input	Calorific value	Life-cycle energy equivalent
Fuel input		
Diesel [a]	42.3 MJ kg^{-1}	50.7 MJ kg^{-1}
Gasoline [b]	32.4 MJ L^{-1}	40.2 MJ L^{-1}
Natural gas [b]	36.6 MJ m^{-3}	38.9 MJ m^{-3}
Material input		
Fertilisers [a]	-	5.88 MJ kg^{-1}
Pesticides [a]	-	475 MJ kg^{-1}
Treated water [a]	-	2.65 MJ t^{-1}
Sodium hydroxide [c]	-	1.5 MJ kg^{-1}
Hydrochloric acid [c]	-	1.70 MJ kg^{-1}

[a] Mourad & Walter (2011)

[b] Huo *et al* (2009)

[c] Hill *et al* (2006)

Of course, variances among LCA studies arise as the choice of the energy unit has a large affect on the energy balance. Pradhan, Shrestha, Van Gerpen, *et al* (2008) considers that life-cycle energy is an understandable unit of measure if the objective is to determine the renewability of biofuel production systems holistically. However, if the goal is to determine process efficiency, the calorific value is more appropriate.

2.1.3 The energy metrics

Energy balances are conducted in life-cycle assessments to determine the renewability of the system. The most popular metrics employed for evaluating the energy balances are the fossil energy ratio (FER) and the net energy ratio (NER) (Liska & Cassman, 2008; Larson & Initiative, 2008).

The FER is the total energy produced in the biofuel relative to the non-renewable fossil-derived energy consumed in the process (Larson & Initiative, 2008):

$$\text{FER} = \frac{\text{Biofuel energy output}}{\text{Fossil fuel energy input}} \tag{2.1}$$

An FER greater than unity indicates that the energy recovered in the biofuel overcomes the non-renewable energy cost of the process. The FER is therefore a measure of the renewability of the system. However, if a portion of the fossil fuel input is replaced with biomass for process energy, the fossil energy ratio fails to account for this (Pradhan, Shrestha, McAloon, Yee, Haas & Duffield, 2011). The net energy ratio (NER) is defined to overcome this shortcoming. The NER determines the quantum of energy produced in the biofuel relative to the fossil energy and biomass-derived energy consumed (Pradhan, Shrestha, McAloon, Yee, Haas & Duffield, 2011):

$$\text{NER} = \frac{\text{Biofuel energy output}}{\text{Fossil fuel energy input} + \text{Biomass energy input}} \tag{2.2}$$

The parameters in the numerator and the denominator are vaguely defined because the definitions vary considerably among studies. The energy metrics may be defined considering the calorific value or the life-cycle energy equivalents of process inputs. The definitions are also dependent on whether mass or energy allocations are applied (Pradhan, Shrestha, Van Gerpen, *et al*, 2008) (as discussed in Section 2.1.4). It is also important to note that the biomass energy input in Equation 2.2 only refers to biomass that is utilised for process electricity and heat production (Castineiras Filho & Pradelle, 2020). It does not refer to the biomass raw material that is upgraded to the biofuel.

The FER and NER are often conflated among studies. Some studies are in agreement with the definition of the FER and NER of Equation 2.1 and Equation 2.2 (Castineiras Filho & Pradelle, 2020; Mourad & Walter, 2011; Pradhan, Shrestha, Van Gerpen, *et al*, 2008; Larson & Initiative, 2008). However, studies, such as Desta, Lee & Wu (2022) and Khatiwada & Silveira (2009), define the NER according to Equation 2.1 (the FER).

2.1.4 Allocation approaches

Allocation methods have been widely used for multi-product biofuel production processes. All of the material and energy inputs are assigned to each co-product based on the mass or energy fractions of the outputs (Morais, Martins & Mata, 2010). A simplified process diagram of soybean to biodiesel is illustrated below to elucidate the application of allocation methods:

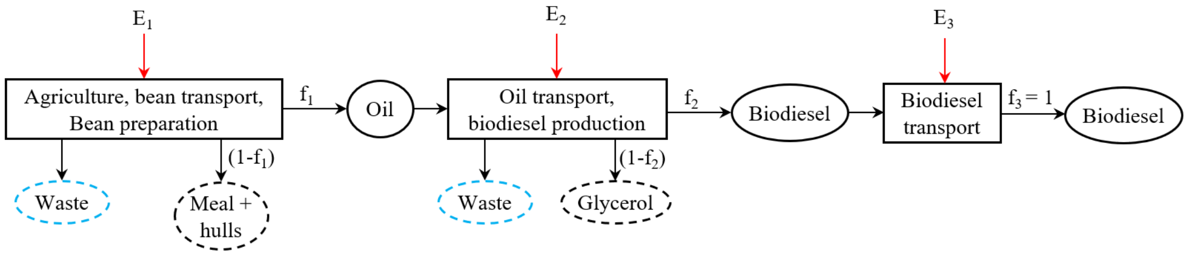


Figure 2.2: A simplified diagram for soybean-biodiesel production to illustrate the use of allocation methods. *The diagram has been adapted from Pradhan, Shrestha, Van Gerpen,* et al *(2008).*

Mass-based allocation is employed to assign energy consumption based on the proportional mass flow of the biofuel or co-product (Pradhan, Shrestha, McAloon, Yee, Haas & Duffield, 2011):

$$E_{\text{biodiesel}} = E_1 \frac{m_{\text{oil}}}{m_{\text{oil}} + m_{\text{meal}}} + E_2 \frac{m_{\text{biodiesel}}}{m_{\text{biodiesel}} + m_{\text{glycerol}}} + E_3 \frac{m_{\text{biodiesel}}}{m_{\text{biodiesel}}}$$

Energy allocation is performed based on the product of the mass and calorific value/life cycle energy equivalent of the respective material flows and divided by the total energy of the outputs (Morais *et al*, 2010):

$$E_{\text{biodiesel}} = E_1 \frac{E_{\text{oil}}}{E_{\text{oil}} + E_{\text{meal}}} + E_2 \frac{E_{\text{biodiesel}}}{E_{\text{biodiesel}} + E_{\text{glycerol}}} + E_3 \frac{E_{\text{biodiesel}}}{E_{\text{biodiesel}}}$$

For the above example, soybean meal and glycerol are significant co-products for soybean-derived biodiesel production. These co-products are sold in separate markets which make up a significant portion of the facility's revenue (Pradhan, Shrestha, McAloon, Yee, Haas & Duffield, 2011). Allocation methods are therefore used to discount the energy consumed by the co-products during processing. For the soybean process specifically, allocation methods assign about 82 % of the fossil energy to the soybean co-products, and only 18 % of the energy consumption to the biodiesel (Patzek, 2009). Using this allocation would, of course, result in inflated values for the NER and FER compared to results where no allocation methods are applied.

This study poses the following question: if the driving goal of biomass cultivation, processing, and refining, is to produce the biofuel, how can we proportion only a fraction of the energy consumption to assess process efficiency? Co-products are sold in separate markets to obtain economic feasibility, rather than energy efficiency. It is for this reason that this study discounts the use of allocation methods entirely for the assessment of process efficiency.

Table 2.2 indicates several results from LCA studies. The differences materialise due to the scope of the system boundary, whether allocation methods are applied, the energy value assigned to material and energy inputs, and the process parameters. Clearly, there is a lack of defined scope for these studies. More so, the foundations of these metric-based evaluations have drawbacks and complexities that obstruct the reproducibility of the results.

Table 2.2: Literature results for the FER and NER for biodiesel and bioethanol production.

Feedstock	Fuel	Energy Metric	Value (No allocation)	Value (Allocation)
Soybean	Biodiesel	NER		0.81 [a]
Soybean	Biodiesel	NER	1.42 [b]	4.27 [b]
Soybean	Biodiesel	FER	4.18 [b]	-
Soybean	Biodiesel	FER	1.84 [c]	5.54 [c]
Soybean	Biodiesel	NER	-	2.51 [d]
Soybean	Biodiesel	NER	-	0.79 [e]
Sugarcane	Bioethanol	NER	0.86–0.95 [f]	-
Sugarcane	Bioethanol	FER	4.2–11.9 [f]	-
Sugarcane	Bioethanol	FER	7.9 [g]	-

[a] Sheehan *et al* (1998)

[b] Mourad & Walter (2011)

[c] Pradhan, Shrestha, McAloon, Yee, Haas & Duffield (2011)

[d] Ahmed, Decker & Morris (1994)

[e] Pimentel & Patzek (2005)

[f] Castineiras Filho & Pradelle (2020)

[g] Von Blottnitz & Curran (2007)

2.2 Other tools for assessing bioenergy systems

In addition to the fossil energy ratio and the net energy ratio, emergy and exergy are popular tools for assessing biofuel conversion processes (Rosen, 2018).

2.2.1 Exergy

Exergy is based on the first and second laws of thermodynamics which is defined as the maximum work that a system produces when it is brought into equilibrium with the environment (Luis & Van der Bruggen, 2014; Velásquez-Arredondo, Junior & Benjumea, 2012). The environment is thus the reference state of evaluation, where exergy is only conserved during reversible processes and is destroyed due to inefficiencies or reversibilities (Luis & Van der Bruggen, 2014). Exergy has been utilised in a number of studies that evaluate the efficiency and environmental impact of biofuel productions processes (Ortiz & Oliveira Jr, 2014; Dewulf, Van Langenhove & Van De Velde, 2005; Shahbeig *et al*, 2022; Velásquez-Arredondo, Junior, *et al*, 2012).

2.2.2 Emergy

Emergy is a measure of the quantum of solar-energy equivalent of all available energy (exergy) that is directly or indirectly consumed to produce a product (Rosen, 2018). Emergy is an environmental accounting method that quantifies the environmental burden required in production systems (Saladini *et al*, 2016). It attempts to quantify the implications of sustainability through the contribution of ecosystems based on thermodynamics (Hau & Bakshi, 2004). All energetic, non-energetic, material, and non-material inflows and outflows are measured according to the same unit, the *solar-equivalent Joule*.

Both exergy and emergy have contributed to the field of work focused on the environmental impact of bioenergy processes. However, they have considerable drawbacks and complexities (Romero & Linares, 2014; Rosen, 2018). They are sensitive to the reference state, the calculations are difficult to apply and interpret, and the metrics fall victim to similar inaccuracies that arise for LCA studies.

2.3 Energy metrics based on the oxygen consumption of fuels

The energy metrics underpinning this dissertation were developed by Merckel *et al* (2019). A brief overview of the research conducted by the author is given for context.

2.3.1 The heat of combustion defined by the mass of oxygen consumed

Merckel, Labuschagne & Heydenrych (2019) evaluated the change in bond dissociation enthalpies of the reduction and oxidation half reactions during the combustion process. It was demonstrated the the reduction of oxygen contributed far more to the quantum of heat liberated during combustion than the oxidation half-reactions. The authors also explored that the oxidation of fuel-bound carbon consumes a portion of the heat liberated during combustion. The oxidation of hydrogen does result in an increase in the exothermicity of the combustion reaction, but only marginally compared to the reduction half-reaction. The authors derived an equation for the heat of combustion, $\Delta_c h^\circ{}_{\text{HHV}}$, from the bond dissociation enthalpies resulting from the combustion reduction and oxidation half-reactions. A simplified and reduced form of the equation is given by Merckel *et al* (2019):

$$\Delta_c h^\circ{}_{\text{HHV}} = \gamma m_{\text{O}_2} \tag{2.3}$$

where $\gamma = -13.87$ MJ $\text{kg}_{\text{O}_2}^{-1}$ and m_{O_2} is the mass of oxygen consumed by the fuel during combustion. The conclusions drawn from this correlation are intuitive yet important: the heat evolved during the combustion process is predominantly determined by the mass of combustible oxygen that the fuel consumes (Merckel, Labuschagne, *et al*, 2019).

Consequently, when converting highly oxygenated biomass feedstocks to biofuels, the goal is to deoxygenate the feedstock to increase m_{O_2}. The pathways that reduce oxygen with sacrificial carbon, mainly CO_2 through decarboxylation and CO through decarbonylation, yield products of higher energy quality (Merckel, Labuschagne, *et al*, 2019). Conserving hydrogen rather than carbon increases the higher heating value of the fuel. The hydrogen to carbon ratio (H/C) should therefore be maximised during biomass-to-biofuel conversion processes.

2.3.2 The change in energy quality as a function of m_{O_2}

Following from the above, Merckel, Labuschagne, *et al* (2020) have developed energy metrics that are based on the calorific value of the biofuel. The metrics presented by the authors allow for a standardised and grounded method to compare biofuel production processes.

For all biomass-to-biofuel systems, the goal is to yield a biofuel of significantly higher calorific value relative to the biomass. If this has been achieved, the quality of the fuel has been improved. The change in energy quality, ΔE_{Q}, evaluates whether there has been an increase in the oxidation potential of the biofuel relative to the feedstock (Merckel, Labuschagne, *et al*, 2020).

ΔE_{Q} is therefore defined as the difference in the higher heating value of the fuel-product, $\Delta_c h^{\circ}|_{\mathrm{HHV,p}}$, and biomass-feed, $\Delta_c h^{\circ}|_{\mathrm{HHV,f}}$, relative to $\Delta_c h^{\circ}|_{\mathrm{HHV,f}}$ (Merckel, Labuschagne, *et al*, 2020):

$$\Delta E_{\mathrm{Q}} = \frac{\Delta_c h^{\circ}|_{\mathrm{HHV,p}} - \Delta_c h^{\circ}|_{\mathrm{HHV,f}}}{\Delta_c h^{\circ}|_{\mathrm{HHV,f}}} \tag{2.4}$$

Based on Equation 2.3, Equation 2.4 may be rewritten in terms $m_{\mathrm{O_2}}$:

$$\Delta E_{\mathrm{Q}} = \frac{m_{\mathrm{O_2|p}}}{m_{\mathrm{O_2|f}}} - 1 \tag{2.5}$$

Subsequently, it can be seen that it is the increase of combustible oxygen of a fuel that gives rise to the improvement of energy quality.

2.3.3 The change in energy yield as a function of $m_{\mathrm{O_2}}$

ΔE_{Q} assesses whether the quality of the biomass feedstock has been improved or reduced. However, Equation 2.4 does not evaluate the quantum of energy that has been transferred from the feedstock to the product. Merckel, Labuschagne, *et al* (2020) addresses this shortcoming by deriving the equation for the change in energy yield, ΔE_{η}:

$$\Delta E_{\eta} = \eta \frac{\Delta_c h^{\circ}|_{\mathrm{HHV,p}}}{\Delta_c h^{\circ}|_{\mathrm{HHV,f}}} \tag{2.6}$$

where η is the mass yield. ΔE_{Q} determines the energy recovery or yield from the biomass. Equation 2.6 may be rewritten in terms of $m_{\mathrm{O_2}}$:

$$\Delta E_{\eta} = \eta \frac{m_{\mathrm{O_2|p}}}{m_{\mathrm{O_2|f}}} \tag{2.7}$$

Therefore, the change in energy yield is both a function of η and ΔE_{Q}, where these two parameters may be used collectively to assess the efficiency of upgradation processes. If the goal of biomass-to-biofuel processes was only to increase η, than the improvement in energy quality would suffer. Of course, this is counterproductive with respect to fuel synthesis pathways (Merckel *et al*, 2019).

Merckel *et al* (2019) and Merckel, Labuschagne, *et al* (2019) evaluated and computed the energy metrics on a theoretical basis for a variety of feedstocks for several biofuels (biocrude, bioethanol, biodiesel, pyrolysis oil, and others). However, for bioethanol and biodiesel specifically, the authors have not taken into account the energy consumption required by the real-processes and did not consider the use of the crop residues for process energy and/or second generation biofuel production. This thesis aims to expand on the author's field of research and address these omissions.

Chapter 3: The process models

3.1 The soybean-biodiesel process model

3.1.1 Soybean characterisation

For processing requirements, soybeans are harvested when they reach their full maturity. At this stage, the desirable soybean seeds have filled the cavity of the pods, the seeds are at the mature pod colour (a light yellow/brown), and the plant has been dried for long enough where the moisture has been reduced to 15 % moisture (Fehr & Caviness, 1977). An illustration of the soybean plant is shown in Figure 3.1:

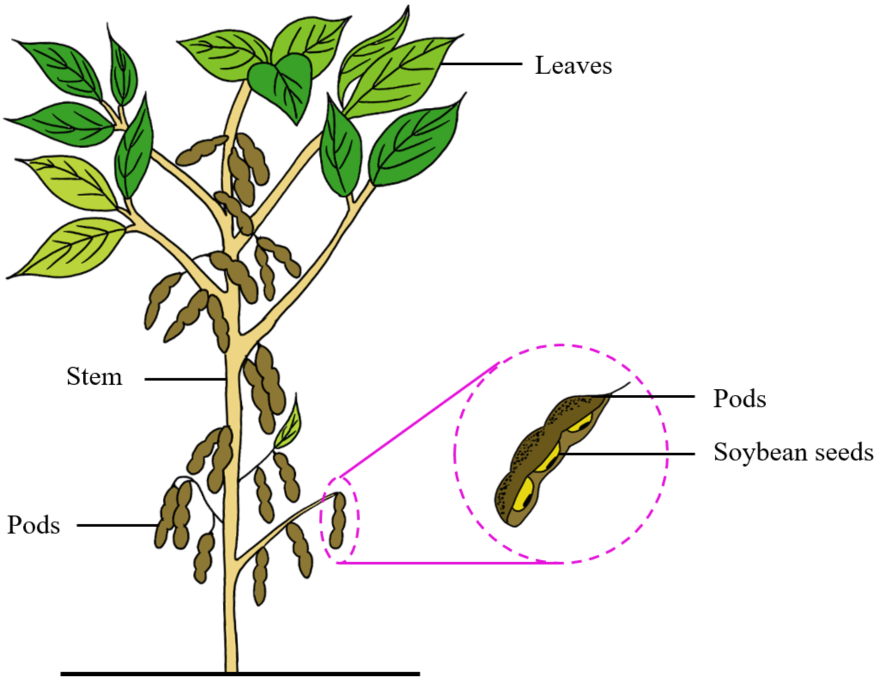


Figure 3.1: The soybean plant. *The diagram has been recreated from Living History Farms (2023).*

Soybean straw/trash embodies the pods, stems, and and leaves that remain after the soybeans have been harvested (Martelli-Tosi *et al*, 2017). The yield of straw varies between 1.2–1.5 kg per kg of soybeans (Martelli-Tosi *et al*, 2017; Bose & Martins Filho, 1984; Lopes *et al*, 2020). The average value of 1.35 kg straw per kg soybeans is used in this study.

The soybean seeds/fruits are mainly cultivated for the production of soybean oil as well as the meal and hulls. The latter are ubiquitously desired for animal feed due to the high protein content of the materials (Banaszkiewicz *et al*, 2011). The hulls are the coatings of the seeds which are removed during the preparation of the seed for oil extraction. The meal is obtained after the crude oil is extracted from the seeds. The composition of the raw soybeans after harvesting is shown in Table 3.1:

Table 3.1: The soybean composition (AR basis), taken from Sheehan *et al* (1998).

Soybean component	Mass %
Oil	18.4
Hulls	7.4
Meal	57.4
Dirt	0.8
Water	16.0

In this study, the soybean co-products (meal and hulls) and waste product (soybean straw) are employed for combustion during cogeneration (depending on the process scenario). The composition of these products are therefore evaluated:

Table 3.2: The ultimate analysis, moisture, and ash content of soybean straw, meal, and hulls. *The ultimate analyses are presented on a dry and ash free basis. All values are reported on a mass basis.*

C (%)	H (%)	O (%)	N (%)	S (%)	Moisture (%)	Ash (%)	Reference
Straw							
45.90	6.60	38.30	8.60	0.60	-	6.45	Ozyuguran, Akturk & Yaman, 2018 [a]
44.64	6.79	47.53	0.94	0.10	9.00	3.54	Jagtap & Kalbande, 2022
47.80	6.90	44.30	1.00	0.10	1.80	4.70	Huang *et al*, 2016
43.80	6.30	48.50	1.40	0.80	5.80	4.70	Motghare *et al*, 2016
Meal							
41.70	6.17	44.99	7.14	-	9.50	6.30	Şensöz & Kaynar, 2006
39.44	5.94	47.70	6.75	0.17	3.24	9.91	Jerzak, Reinmöller & Magdziarz, 2022
Hulls							
42.57	5.31	49.93	2.12	0.07	7.75	5.21	Oliveira, Cardoso & Ataide, 2015 [a]
41.50	5.70	51.10	1.60	0.10	6.50	4.60	Emiola-Sadiq, Zhang & Dalai, 2021
45.14	6.48	46.29	1.88	0.21	-	4.30	Parmar, 2017 [a]

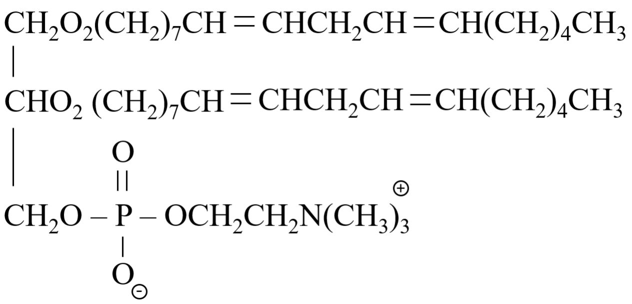
[a] Ultimate analysis corrected and normalised to be on a dry and ash free basis

The soybean oil is the desirable feedstock for biodiesel production. The composition of raw soybean oil is described in Table 3.3:

Table 3.3: Soybean oil composition, taken from Sheehan *et al* (1998)

Soybean component	Mass %
Triglycerides	95.20
Phospholipids (Gums)	2.50
Unsaponifiable matter	1.60
Free fatty acids	0.70

To determine the composition of the oil, each component is characterised. The phospholipids, also known as gums or lecithin, occur in all vegetable oils, where soybean oil has the largest portion of its oil made up of lecithin (Erickson, 2015: 174). The phospholipids in soybean oil are predominantly composed of C_{16} to C_{18} acid phospholipids, similar to the triglyceride component of the oil (Erickson, 2015: 18). The gum in the oil is modelled as the highest occurring phospholipid in the oil: diacylphosphatidyl choline (Liu & Ma, 2011). The R-groups are assumed to be derived from linoleic acid.



$$\begin{array}{l} CH_2O_2(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3 \\ | \\ CHO_2\,(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3 \\ | \\ CH_2O - \overset{\overset{\displaystyle O}{||}}{\underset{\underset{\displaystyle O^{\ominus}}{|}}{P}} - OCH_2CH_2\overset{\oplus}{N}(CH_3)_3 \end{array}$$

Figure 3.2: Phospholipids in oil modelled after diacylphosphatidyl choline with linoleic acid R groups. *The figure has been recreated from Erickson (2015: 20).*

The unsaponifiable matter in soybean oil is modelled as β-sitosterol which occurs in the highest concentration of the unsaponificable component (Erickson, 2015; Granjo, Duarte & Oliveira, 2017: 24). β-sitosterol has a a molecular formula of $C_{29}H_{50}O$ (PubChem, 2023a). The predominant fatty acids in soybean oil are palmatic, stearic, oleic, linoleic, and linolenic acid, where linoleic acid occurs in the highest concentration in soybean oil (Priolli *et al*, 2015; Medic, Atkinson & Hurburgh, 2014; Panthee, Pantalone & Saxton, 2006). The free fatty acid component of soybean oil is assumed to be made up of linoleic acid for simplicity, with a composition of $C_{18}H_{32}O_2$ (PubChem, 2023b). Similarly, the triglyceride content of soybean oil is considered to be composed of trilinolein with a molecular formula of $C_{57}H_{98}O_6$ (PubChem, 2023c; Granjo *et al*, 2017). The elemental composition of the raw oil was calculated based on the composition of the raw oil in Table 3.3 and the components after which the oil is modelled:

Table 3.4: Soybean raw oil elemental composition. *The values are presented on a daf basis and as a mass %.*

Oil component	Modelled component	Total (%)	C (%)	H (%)	O (%)	N (%)	P (%)
Triglycerides	Trilinolein	95.20	77.90	11.16	10.93	0.00	0.00
Phosphatides (Gums)	Lecithin	2.50	68.02	10.08	15.11	1.89	4.18
Unsaponifiable matter	β-sitosterol	1.60	84.06	12.08	3.86	0.00	0.00
Free fatty acids	Linoleic acid	0.70	77.14	11.43	11.43	0.00	0.00
Total oil		100.00	77.75	11.17	10.93	0.05	0.10

Based on the above compositions, the average ultimate analysis for the entire plant is determined:

Table 3.5: Ultimate anlalysis for soybean straw, hull, meal, and raw oil. *The values are presented on a daf basis and as a mass %.*

Constituent	Total (%)	C (%)	H (%)	O (%)	N (%)	S (%)	P (%)
Straw	61.95	45.44	6.64	45.55	2.97	0.40	0.00
Meal	25.24	40.54	6.05	46.31	6.94	0.32	0.00
Hull	3.35	43.07	5.83	49.11	1.87	0.12	0.00
Oil	9.46	77.75	11.17	10.93	0.05	0.00	0.10
Total plant	100.00	47.18	6.89	41.96	3.66	0.30	0.01

3.1.2 Process overview of soybean-biodiesel

The body of literature regarding the production of biodiesel from soybean oil is quite expansive. However, there are few models that evaluate the entire biorefinery for the soybean-biodiesel process. To the best of the author's knowledge, the only studies that provide exhaustive mass and energy balances are those from Sheehan *et al* (1998), Granjo *et al* (2017), De Pretto, Tardioli & Costa (2017), and Haas *et al* (2006). That being said, Haas *et al* (2006) presents a techno-economic study where the developed model is unavailable and the mass and energy balances are not outlined. Furthermore, Haas *et al* (2006) only considers biodiesel production from degummed oil as the feedstock (rather than the soybeans). The process model developed by De Pretto *et al* (2017) heavily cites parameters given by Granjo *et al* (2017). However, Granjo *et al* (2017) is almost completely based on data presented by Sheehan *et al* (1998). Consequently, the only reliable model for soybean-biodiesel production is from Sheehan *et al* (1998). There is a serious gap in literature for the biodiesel production process from soybeans, especially considering that Sheehan *et al* (1998) based their model on existing biodiesel refineries in 1998, where technology has since improved.

Regardless, most of the parameters used for the development of the biodiesel production process from soybeans are taken from Sheehan *et al* (1998), unless otherwise indicated. Some of the parameters are amended. A summary of the main parameters for the model development are given in Appendix A. The proceeding subsections elucidate the biodiesel production process, where an overview is shown in Figure 3.3.

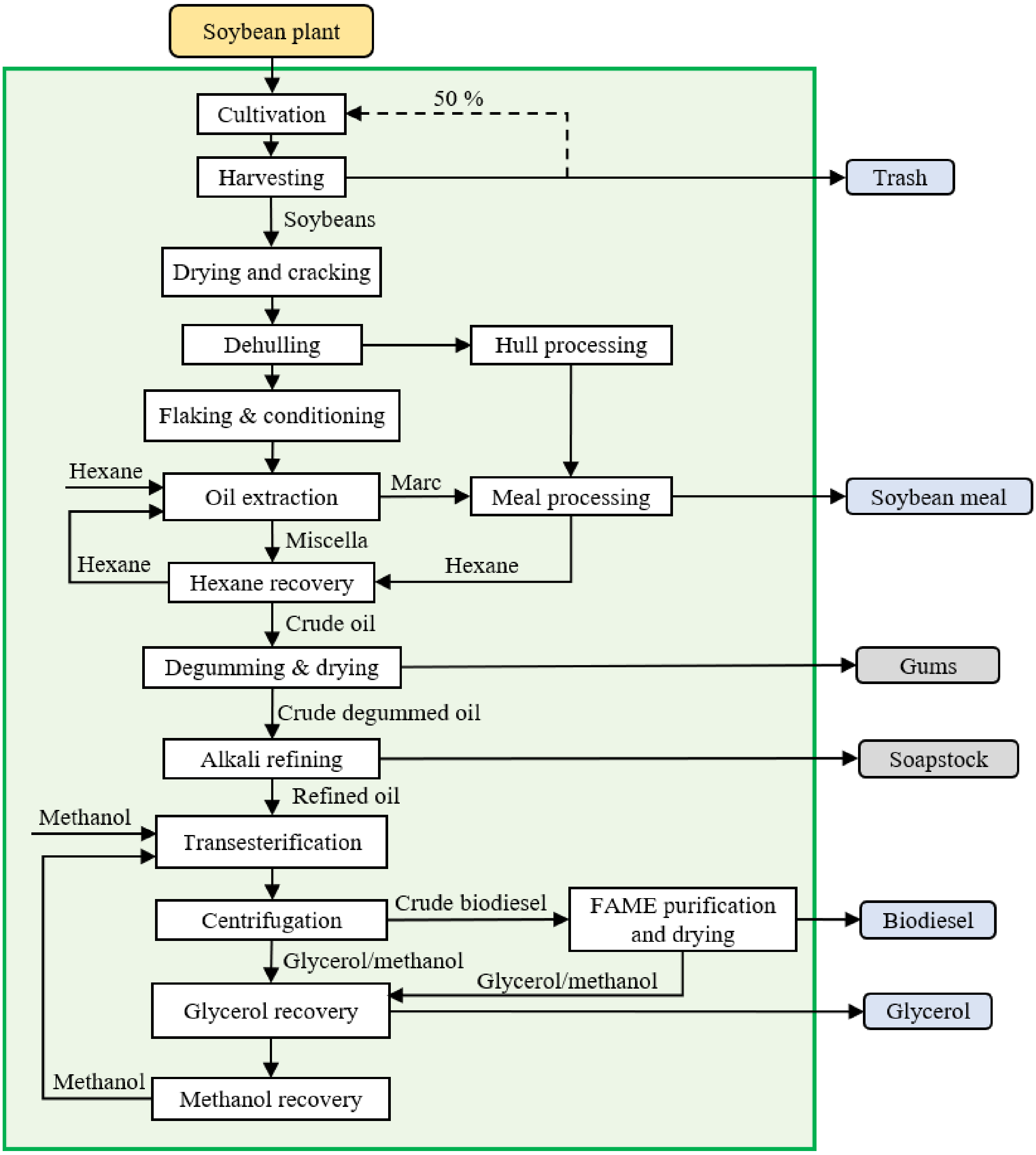


Figure 3.3: The biodiesel production process. *The diagram has been adapted from Pradhan, Shrestha, McAloon, Yee, Haas, Duffield & Shapouri, 2009.*

3.1.3 Soybean cultivation and harvesting

The fossil energy consumption for the cultivation and harvesting of soybeans is evaluated in various life-cycle assessment studies. However, the agricultural requirements in these studies account for all energy inputs in terms of the life-cycle energy equivalent of the inputs. These include the energy associated with fertilisers, pesticides, lime, seeds, labour requirements, infrastructure, and for transportation between different stages. The system boundary of this thesis is only concerned with direct energy consumption of the processing requirements. Therefore, the only energy inputs for cultivation and harvesting taken into account include:

- Fuel required for field equipment (*e.g.*, tractors and combines) which does not include transportation between the fields and refinery.
- Direct energy utilised for activities such as irrigation.
- Fossil fuels consumed as a direct utility for cultivation and harvesting.

Within these limitations, the energy inputs per hectar and the soybean yield are outlined in Table 3.6:

Table 3.6: Energy inputs for soybean cultivation.

Input	Unit	Ref. 1	Ref. 2	Ref. 3	Ref. 4			
					State 1	State 2	State 3	State 4
Diesel	L ha^{-1}	49.48	33.3	38.8	47.6	49.4	55.1	62.8
Gasoline	L ha^{-1}	29.09	12.8	35.7	-	-	-	-
LP gas	L ha^{-1}	3.55	2.00	3.30	-	-	-	-
Natural gas*	Nm^3 ha^{-1}	0.0049	4.10	-	-	-	-	-
Electricity	kWh ha^{-1}	4.60	17.10	10.00	-	-	-	-
Soybean yield	kg ha^{-1}	2556	2906.7	2668	2930	2970	2940	2340

* Volume of gas is assumed to be in normal m^3 — 0 °C and 1 bar

Ref. 1 Sheehan *et al* (1998)

Ref. 2 Pradhan, Shrestha, McAloon, Yee, Haas & Duffield (2011)

Ref. 3 Pimentel & Patzek (2005)

Ref. 4 Castanheira *et al* (2015)

The energy inputs from Table 3.6 are converted to the unit of MJ per tonne soybeans (MJ $t_{beans}{}^{-1}$)—the higher heating value (HHV) of the fuels used for this calculation are given in Table 3.7. The density of natural gas was taken at 0 °C and 1 bar.

Table 3.7: Density and HHV of fossil fuels. *The values were taken from Wang (2008).*

Fuel	HHV (MJ kg^{-1})	Density (kg m^{-3})
Diesel	45.77	836.6
Gasoline	46.54	744.7
LPG	50.15	508.0
Natural gas	52.23	0.777

The average energy consumption for the cultivation and harvesting of soybeans is -922.75 MJ t_{beans}^{-1}. During harvesting, it is assumed that 50 wt. % of the trash is left on the field for soil conservation, similarly to the sugarcane industry (De Pretto *et al*, 2017).

3.1.4 Soybean oil and meal production

Bean preparation

After harvesting the soybeans, they are screened to remove the dirt and dried to reduce the moisture which improves the cracking efficiency. The energy consumption for drying given by Sheehan *et al*, 1998 is far beyond what is reasonably possible (natural gas energy of -1114 MJ t_{beans}^{-1}). The theoretical energy required to reduce the moisture content by 5.5 wt. % was calculated using the latent heat of vaporisation of water. This energy consumption is 5x the theoretical value and is inline to a drying operation where all of the bean moisture is removed. A more reasonable measure of drying energy is taken from Erickson, 2015: 71 (-218 MJ t_{beans}^{-1}, which equates to a drying efficiency of 82 %).

The beans are then tempered in storage bins to assist with the detachment of the hulls (Granjo *et al*, 2017). The soybeans are cracked in a series of crushing rollers and the hulls are separated from the seeds with screens and aspirators (Sheehan *et al*, 1998; Granjo *et al*, 2017). The separation is not perfect where a fraction of meal, oil, and moisture is carried over with the hulls. The beans are then sent to a conditioner to further reduce the moisture content and heat up the beans. The beans are then flaked with roller mills to reduce the particle size which promotes the extraction of the oil (Sheehan *et al*, 1998; Granjo *et al*, 2017).

Oil extraction

Oil extraction from soybeans can be accomplished using mechanical extruders or extraction with solvents (Rajaeifar *et al*, 2014). Extraction with organic solvents, namely hexane, is the predominant method used for soybean oil recovery and is therefore considered in this process model (Erickson, 2015: 65).

The soybean flakes are fed into a counter-current extraction unit where hexane is used to dissolve the soybean oil (Pradhan, Shrestha, McAloon, Yee, Haas, Duffield & Shapouri, 2009; Sheehan *et al*, 1998). The miscella and the marc stream exit the extractor. The miscella is the oil-laden hexane stream which is sent to evaporators for hexane recovery. It is assumed that there is no moisture or hulls in the miscella. The marc consists of the soybean meal and hexane (Granjo *et al*, 2017). It is assumed that all the flake moisture, remaining hulls, and unrecovered oil remain in the soybean flake stream. Most of the solvent is recycled, with a small amount of make-up hexane consumed during extraction (Sheehan *et al*, 1998). Some hexane is vented from the extractor which is recovered in the downstream process. The mass balance indicates that 7.12 wt. % of the hexane is vented. The make-up hexane is considered as an energy utility into the process.

Meal and hull processing

The flakes (marc stream) are sent to a desolventiser-toaster which removes the hexane and toasts the flakes using indirect steam (Granjo *et al*, 2017). The hexane rich stream is sent to the solvent recovery unit. Open steam is also used to increase the moisture of the flakes (Sheehan *et al*, 1998). It is assumed that all of the hexane is removed from the marc stream. The soybean meal is then dried to reduce the moisture content to 14 wt. %, cooled to further reduce the moisture, and then ground and stored (Sheehan *et al*, 1998). The hulls from the dehuller are also toasted, ground, and combined with the soybean meal (Sheehan *et al*, 1998).

Oil recovery

The miscella from the extraction process is sent to multiple effect evaporators to concentrate the oils. Heat integration is used for the first effect evaporator where the vented hexane vapour from the desolventizer-toaster is used for evaporation of the hexane in the miscella (Sheehan *et al*, 1998). Steam is used for the second and third effect evaporators. The hexane from the miscella is recovered – 100 % recovery is assumed and no oil losses are assumed to occur.

Solvent recovery and waste treatment

The hexane from all of the hexane-containing streams is recovered in a settling tank. The water phase is also sent for treatment to recover the remaining hexane. These two operations are combined for the sake of simiplicity which does not affect the mass and energy balance. A small amount of hexane losses occur: 0.20 wt. % (Sheehan *et al*, 1998). The recovered hexane is recycled to the oil extraction process. The make-up hexane is regarded as an energy input.

3.1.5 Oil refining

A refining step is employed to remove undesirable compounds, namely the gums and the free fatty acids (FFAs). Degumming is first performed to remove the phosphatides, and thereafter, physical or chemical refining can be employed to reduce the FFA content to an acceptable level ($<$0.05 wt. %) (Meira *et al*, 2015; Čmolík *et al*, 2000). Chemical refining is considered in this study.

Oil degumming

The natural gums (phospholipids) in crude soybean oil are removed to prepare the oil for storage and caustic refining (Erickson, 2015: 175). Phosphotides in soybean oil are hygroscopic; when hydrated, the gums precipitate out of the oil forming a sludge (Erickson, 2015: 175). This behaviour is used to degum the oil. Crude soybean oil is mixed with hot water in a hydration tank causing them to swell where they can be removed via centrifuging (Sheehan *et al*, 1998). The gums are assumed to be completely recovered, where they are then sent to the desolventizer-toaster and mixed with the meal (Sheehan *et al*, 1998).

The total oil losses to the gum stream amount to 3.11 % (Sheehan *et al*, 1998). The triglycerides and phosphatides contribute to 0.476 % and 2.50 % of the total oil losses respectively. The balance of the oil losses are assumed to come from the unsaponifiable matter. The composition of the crude, degummed oil is shown in Table 3.8:

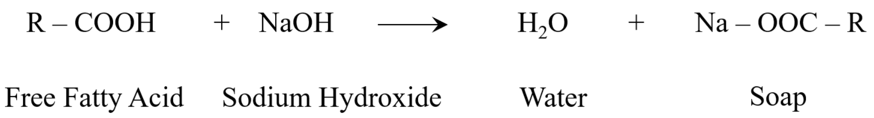
Table 3.8: Composition of crude, degummed oil. *The composition is calculated from the mass balance model with the relevant assumptions.*

Component	Mass %
Triglycerides	97.76
Phosphatides	0.00
Unsaponifiable matter	1.51
Free fatty acids	0.72

The oil is vacuum dried and sent to storage. The total yield of the oil up to this point is 92.5 wt. % from the soybeans, and the triglyceride yield is 95.0 wt. %.

Alkali refining

A high FFA content will result in a reaction with an alkali catalyst to produce soap, as shown in Figure 3.4 (Chang & Liu, 2010).



$$R - COOH + NaOH \longrightarrow H_2O + Na - OOC - R$$

Figure 3.4: Saponification of Free Fatty Acids.

Saponification of the triglycerides may also occur according to the reaction described in and Figure 3.5.

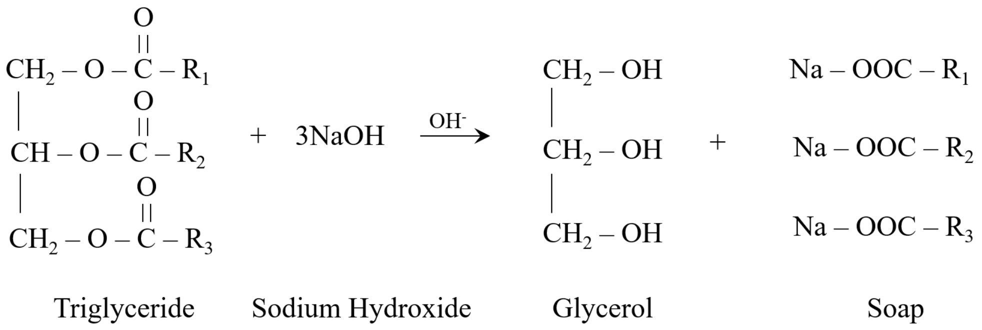


Figure 3.5: Saponification of triglycerides.

Water also inhibits the reaction and results in the production of FFAs as well promoting saponification (Atadashi *et al*, 2012), as shown in Figure 3.6:

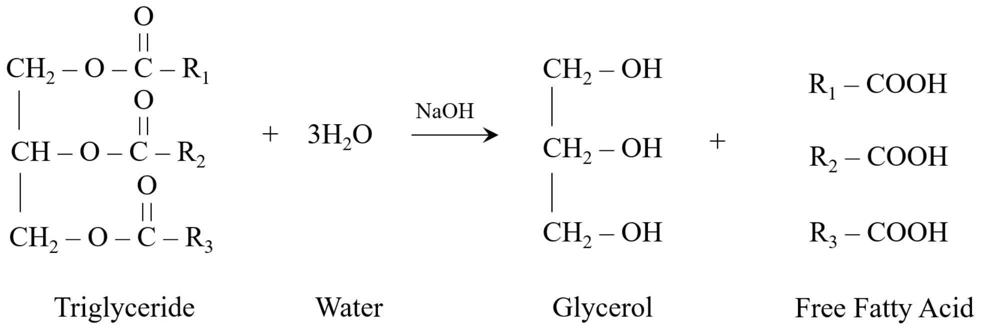


Figure 3.6: Reaction between triglyceride and water.

The production of soap during transesterification reduces the biodiesel yield, demands additional purification steps (Atadashi *et al*, 2012) and the separation of soap from biodiesel is more difficult (Sheehan *et al*, 1998; Myint & El-Halwagi, 2009).

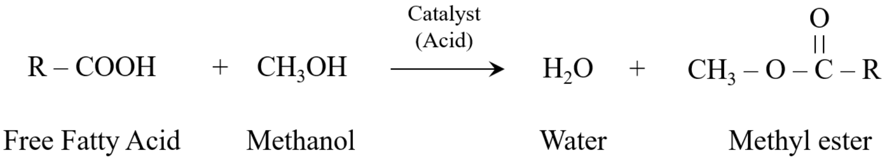
Consequently, feedstocks with higher water (>0.06 %) and FFA contents need to undergo pretreatment steps before undergoing transesterification with alkali catalysts (Atadashi *et al*, 2012). Alkali refining of the crude oil is an established practice in industry to remove the FFAs so that the saponification reaction is minimised. The crude oil is then dried before entering the transesterification reactor (Nasir *et al*, 2013).

Soybean oil is heated to 70 °C and mixed with 14 °Baume (9.5 wt. %) caustic solution where FFA and soap are formed (Sheehan *et al*, 1998). The NaOH is added in a 113 % stoichemitric excess of the FFAs (Sheehan *et al*, 1998). This equates to about 2.38 wt. % of the crude oil containing 0.72 wt. % FFAs. (Erickson, 2015: 184). Wash water heated to 70 °C is also added at 15 wt. % of the soybean oil (Sheehan *et al*, 1998). The oil/-soap/water mixture is sent through a centrifuge to retrieve the oil. Most of the FFAs are removed, where the oil losses are fully described in Table A.1.3. Triglycerides are lost due to the saponification reaction shown in Figure 3.5. The soapstock is considered as a waste stream.

Vegetable oils marketed for consumption must undergo further refining to achieve the correct colour and taste for customers (Gharby *et al*, 2022). For the production of food-grade oil, the oils recovered after alkali refining are usually bleached, dewaxed, and deodorised to eliminate the pigment, waxes, volatiles, and further reduce the FFA content (Gharby *et al*, 2022). Some studies assessing the soybean-biodiesel production process have modelled these refining stages (Granjo *et al*, 2017; De Pretto *et al*, 2017). However, these operations are not necessary for biodiesel production where the vegetable oil is not marketed as an edible product: it is only important to undergo degumming and neutralisation (alkali refining) for biodiesel production (Dunford, 2016). Therefore, only these steps are modelled.

3.1.6 Biodiesel production

Industrially, biodiesel may be produced from vegetable oil using transesterification of the triglycerides or by esterification of the free fatty acids (Salvi & Panwar, 2012). These are two complimentary synthesis pathways. Esterification is the reaction of a short-chain alcohol, usually methanol, with a free fatty acid forming water and methyl ester, as defined in Figure 3.7. Esterification is an alternative reaction to transesterification, which is normally employed for low-quality vegetable oils that have a high FFA content (> 3 wt. %), such as waste cooking oil, animal fats, and jatropha seed oil (Borges & Díaz, 2012; Chongkhong *et al*, 2012). An acidic catalyst is used in the reaction to circumvent the saponification of the FFAs.



$$R - COOH + CH_3OH \xrightarrow{\text{Catalyst (Acid)}} H_2O + CH_3 - O - \overset{\overset{\displaystyle O}{||}}{C} - R$$

Figure 3.7: Esterification reaction.

Crude soybean oil is a high quality oil with an FFA content of less than 1 wt. %. As a result, the esterification reaction is not advantageous to maximise the biodiesel yield. The free fatty acids are also largely removed during the alkali refining step. The esterification reaction of FFAs is therefore not considered in this study.

Soybean oil is industrially converted to biodiesel through transesterification. The acid/alkali catalysed reaction occurs between the triglycerides and a short-chain alcohol (usually methanol) (Fernando *et al*, 2007). The reaction produces biodiesel, comprising of three fatty acid esters (FAME), and the valuable co-product glycerol (Fernando *et al*, 2007). The overall reaction is shown in Figure 3.8:

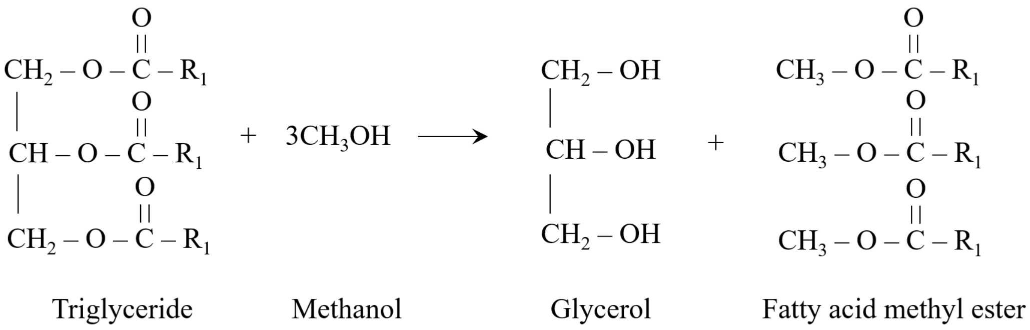


Figure 3.8: Transesterification reaction.

Transesterification can be performed using either homogenous or heteregenous catalysts, where the catalyst can be either acidic or alkali. Alkaline catalysts are suitable for oils (such as soybean oil) that have a free fatty acid content of less than 3 % and a low moisture content (Selvaraj, Praveenkumar & Moorthy, 2019). Transesterification reactions with alkaline catalysed have reaction times that are up to 4000 times faster and higher biodiesel yields achievable than those that are acid catalysed making this method the more conventional biodiesel production method (Fukuda, Kondo & Noda, 2001; Rincón, Jaramillo & Cardona, 2014). The alkaline catalysts are conventionally sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide ($NaCH_3OH$), or potassium methoxide (KCH_3OH) (Verma & Sharma, 2016). Sodium methylate as a catalyst has been shown to reach higher yields, however, sodium hydroxide achieves high yields in a much shorter reaction time than sodium or potassium methylate (Myint & El-Halwagi, 2009). NaOH and KOH are also cheaper, more available, and are more widely used on an industrial scale than the counter-parts (Verma & Sharma, 2016). For the short-chain alcohol, methanol is usually employed over ethanol due to its considerably lower cost, greater ease of recovery of the alcohol for recycling, and greater reactivity (Fukuda *et al*, 2001; Haas *et al*, 2006; Verma & Sharma, 2016). For this study, the transesterification using methanol and NaOH catalysed is employed. Some process models take into account the saponification reaction during transesterification (Myint & El-Halwagi, 2009), whereas others do not (Haas *et al*, 2006; Zhang *et al*, 2003; Sheehan *et al*, 1998). For the sake of simplicity, only the transesterification reaction in Figure 3.8 is considered.

According to the ASTM standards, biodiesel must have a purity > 99.65 % (Myint & El-Halwagi, 2009; Zhang *et al*, 2003) and glycerol must have a purity of above 90 % to be markatable as a refined product. Purification steps are therefore required for these products. The main operations during biodiesel production are 1) transesterification 2) FAME recovery and purification and 3) glycerol and methanol purification (Myint & El-Halwagi, 2009).

Transesterification

For the mass balance of the transesterification reaction, the refined oil was modelled as trilinolein having a molecular formula of $C_{57}H_{98}O_6$ (PubChem, 2023c). Therefore, the R group is $C_{17}H_{31}$. FAME therefore has a formula of $C_{57}H_{102}O_6$, which is verified by checking that the transesterification reaction balances.

Stoicheometrically, 3 moles of methanol are required per mole of trilinolein. However, an excess of methanol is used to obtain higher yields—a 6:1 molar ratio of methanol:oil (twice the stoicheometric amount) at 60 °C and 1 wt. % NaOH of the oil (Zhang *et al*, 2003; Myint & El-Halwagi, 2009; Freedman, Pryde & Mounts, 1984). These operating conditions achieve an optimal conversion of triglycerides (93 %–99 %) within 1 h at the most commercially viable quantities (Freedman, Butterfield & Pryde, 1986; Chang & Liu, 2010; Sheehan *et al*, 1998). The transesterification reaction occurs in two continuously stirred tank reactor (CSTR) in series, where the overall conversion is assumed to be 99 wt. %, as reported in Sheehan *et al* (1998) and Freedman, Pryde, *et al* (1984). Performing the reaction and mass balance confirms that the FAME:glycerol mass production is 9.59:1. For a 6:1 methanol to oil stochemoetric ratio, methanol is added in 21.87 wt. % of oil.

After each CSTR, there is a settling tank (2 in total) where the aqueous phase of the mixture from each tank is sent to the glycerol recovery section. The final oil phase from the second settling tank is sent for purification of FAME. It is assumed that the FAME (with the oil) is completely recovered with some carry over (5 wt. %) of the aqueous phase (mixture of glycerol and methanol). The energy consumed in the transesterification stage is associated with heating up the reactants to 60 °C.

FAME purification

The mass balance for FAME purification is evaluated on an overall basis. The methyl ester rich phase is washed in counter-current columns to remove water-soluble compounds, namely methanol and glycerol (Sheehan *et al*, 1998). Water at 70 °C is fed at 20 wt. % of FAME. 10 % of the water is carried over with the ester rich product (the FAME and oil are completely recovered). The balance of water and most of the methanol and glycerol exit the bottoms and are sent to the recovery section. The ester phase enters a settler to separate the aqueous phase which is also sent for recovery. The ester rich phase is then preheated and vacuum dried to remove all the remaining methanol, glycerol, and water (Sheehan *et al*, 1998).

The biodiesel product composition in shown in Table 3.9. The overall yield of biodiesel is 15.59 tonne per tonne of soybeans.

Table 3.9: Composition of biodiesel product

Component	Mass %
FAME	98.97
Triglycerides	1.00
Unsaponifiable matter	0.03
FFAs	<0.01

Glycerol and methanol recovery

The glycerol/methanol rich streams are recovered from the settlers after the transesterification reactors, the ester wash columns, and the vacuum dryers. First, the glycerol/methanol rich streams are preheated and distilled to recover the methanol in the distillate and the glycerol in the bottoms (Sheehan *et al*, 1998)—100 % recovery of the methanol and glycerol in the distillate and bottoms respectively is assumed. The bottoms product is mixed with a 10 wt. % HCl solution to convert any remaining soaps to FFAs which can be removed via centrifuging. The FFAs are considered to be waste (Haas *et al*, 2006). The glycerol stream contains 20 wt. % water at this stage which making it suitable for sale as crude glycerol (Haas *et al*, 2006).

The methanol stream is sent to a subsequent distillation column to purify the methanol to recycle to the transesterification reactors. The overall recovery is 99 wt. % of methanol. The water recovered from this section is recycled to the ester wash columns (Haas *et al*, 2006; Sheehan *et al*, 1998).

3.2 The sugarcane-bioethanol process model

3.2.1 Sugarcane characterisation

For bioethanol production, the sugarcane is cultivated to harvest the stalk. The stalk contains both the saccharide-rich juices and the bagasse. The extracted sugar is fermented to bioethanol in first generation (1G) bioethanol production. Sugarcane bagasse is the lignocellulosic residue that remains after the juice has been extracted (Bizzo *et al*, 2014). The sugarcane trash/straw consists of green leaves, dry leaves, and green tops that is left after the stalk is harvested (Carvalho *et al*, 2020; Oliveira, Nascimento, *et al*, 2014).

An illustration of the sugarcane plant is shown in Figure 3.9.

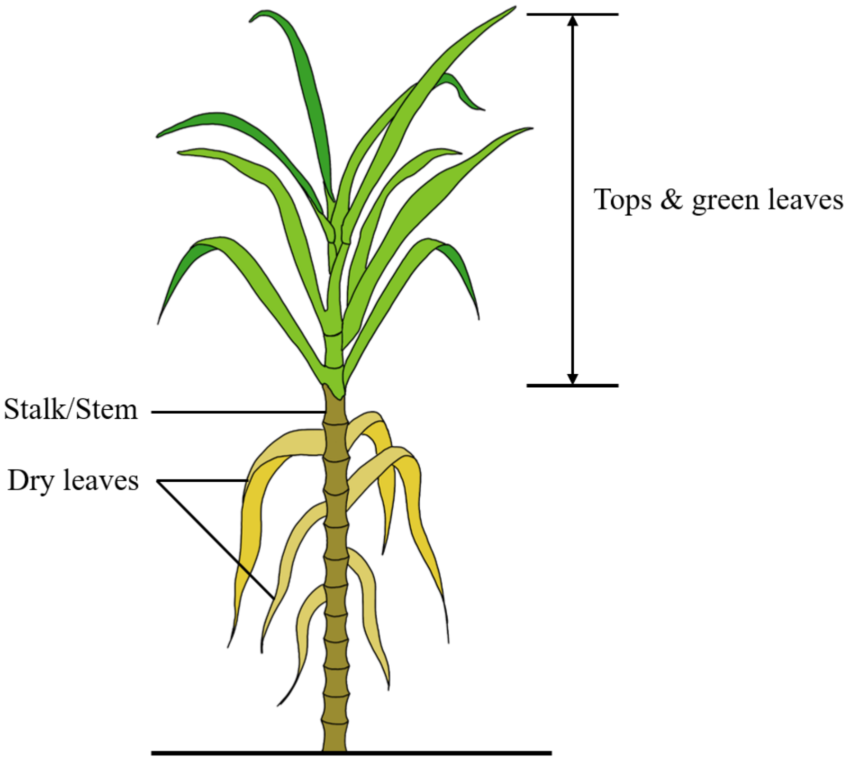


Figure 3.9: The sugarcane plant. *The diagram has been recreated from Calderan-Rodrigues* et al *(2021) and Bizzo* et al *(2014).*

The composition of the sugarcane stalk received in the biorefinery is presented in Table 3.10:

Table 3.10: Composition of the sugarcane stalk (AR basis). *The composition is taken from Dias, Ensinas,* et al *(2009) and Furlan, Costa,* et al *(2012).*

Sucrose (%)	Glucose (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Water (%)	Dirt (%)	Impurities/ash (%)
13.30	0.62	4.77	4.53	2.62	71.57	0.60	1.99

Both the sugarcane trash and the bagasse are produced in large quantities. On average, 200–280 kg of bagasse (wet basis) is produced per tonne of sugarcane (Morris, Waldheim, *et al*, 2001) and 140 kg of trash (dry basis) is produced per ton of sugarcane harvested (Bizzo *et al*, 2014). The composition of the straw and bagasse considered in this study is shown in Table 3.11.

Table 3.11: Composition of the sugarcane trash and bagasse. *The compositions are presented on a dry basis and as a mass %.*

Component	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)	Ash (%)
Trash [a]	31.46	27.03	31.14	8.90	1.47
Bagasse [b]	39.00	37.00	21.00	0.00	3.00

[a] Carvalho *et al* (2020)

[b] Furlan, Costa, *et al* (2012)

To perform the mass and energy balance of the bioethanol production process, the biomass constituents are characterised, as shown in Table 3.12:

Table 3.12: Characterisation of sugarcane constituents.

Component	Molecular formula
Sucrose	$C_{12}H_{22}O_{11}$
Glucose	$C_6H_{12}O_6$
Cellulose [a, b]	$C_6H_{10}O_5$
Hemicellulose (xylan) [a, b]	$C_5H_8O_4$
Lignin [b]	$C_{10}H_{11.6}O_{3.9}$

[a] Ortiz & Oliveira Jr (2014)

[b] Dias, Junqueira, Cavalett, Cunha, Jesus, Rossell, *et al* (2012)

The moisture content of the biomass streams is material for the valorisation or combustion process for 2G bioethanol or cogeneration, respectively. Bagasse is produced with 50 wt. % moisture directly from the sugarcane mill (Carvalho *et al*, 2020; Furlan, Costa, *et al*, 2012; Almeida & Colombo, 2021). For the sugarcane straw, the dry leaves makes up 60 wt. % of the total straw and the balance is the green leaves and tops (Menandro *et al*, 2017). The average moisture content of the trash is around 50 wt. %, as reported by Bizzo *et al* (2014), Braunbeck *et al* (1999), and Sartori *et al* (2001). However, after being left to dry in the fields for 2 weeks, the moisture content drops to about 15 wt. % (Bizzo *et al*, 2014). Consequently, a moisture content of 15 wt. % for the trash is assumed in the model.

3.2.2 Process overview of sugarcane-bioethanol

A simplified diagram of bioethanol production is shown in Figure 3.10. The authors of Dias, Ensinas, *et al* (2009) have published several papers to evaluate bioethanol production from sugarcane. These include heat-integration, techno-economic, environmental, and optimisation studies that have assessed different first generation (1G), second generation (2G), and integrated 1G and 2G scenarios using different methods of valorisation. The authors have been extensively cited in several papers that present models with agreeable parameters. This study is heavily based on the model presented by Dias, Ensinas, *et al* (2009) for the 1G process, and Dias, Junqueira, Cavalett, Cunha, Jesus, Rossell, *et al* (2012) and Dias, Junqueira, Rossell, *et al* (2013) for the 2G process. Even so, the model parameters presented by the authors have been reviewed and compared with other publications that present similar analyses. In this way, this study employs a combination of literature parameters to develop a unique model for 1G and 2G bioethanol production.

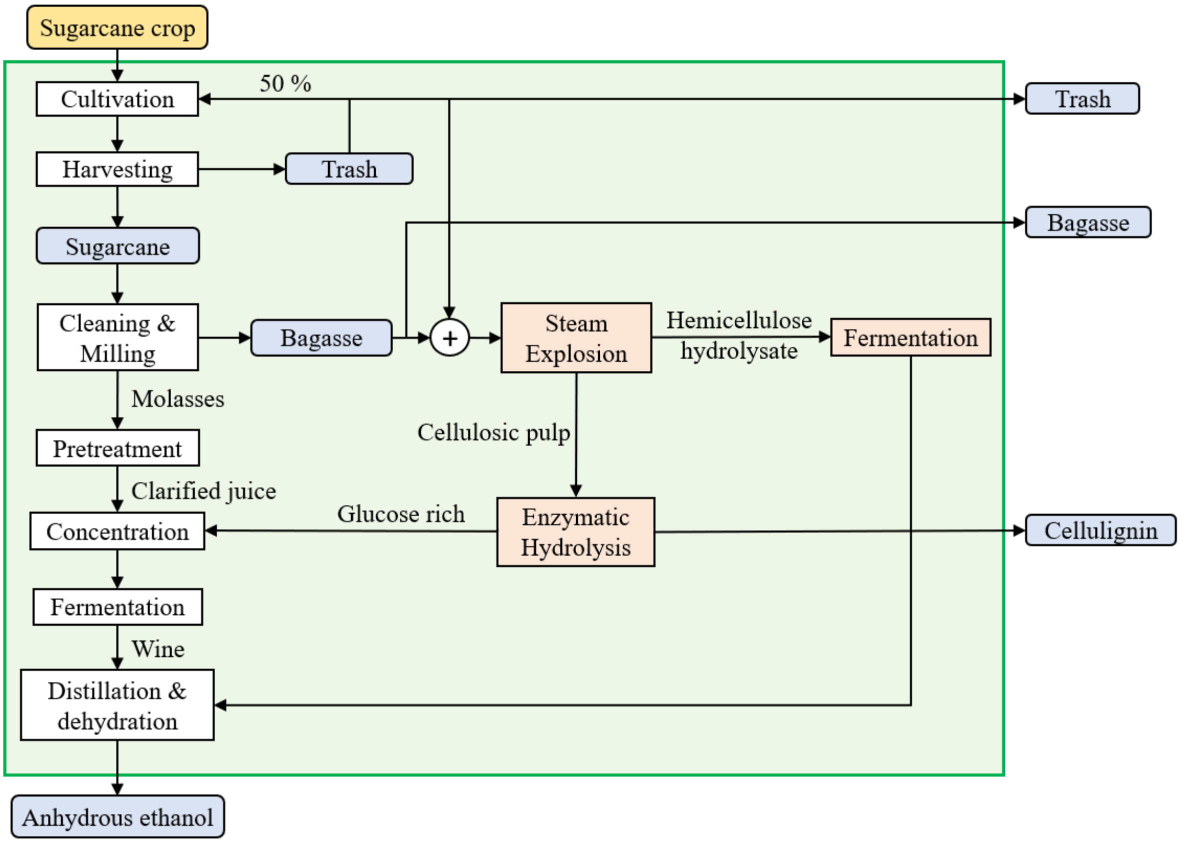


Figure 3.10: Process overview of 1G and 2G bioethanol production from sugarcane. *The white and orange blocks represent the operations for 1G and 2G bioethanol respectively. The blue blocks are the final and co-products of the process.*

The parameters used for the model development are presented in Appendix B. The proceeding subsections provide a detailed explanation of the unit operations considered that supplement the simplified diagram of Figure 3.10.

3.2.3 Sugarcane cultivation and harvesting

As with Section 3.1.3, the energy consumption considered for the cultivation and harvesting of the sugarcane stalk are those associated with the processing and field requirements.

The most comprehensive studies identified, that present fossil fuel consumption data for sugarcane agricultural and cultivation activities, are those by Macedo, Seabra & Silva (2008) and Tsiropoulos *et al* (2014).

Table 3.13: Energy inputs for sugarcane cultivation and harvesting.

Input	Unit	Macedo, Seabra & Silva (2008)	Tsiropoulos *et al* (2014)
Diesel	L ha^{-1}	317.10	314.34
Sugarcane yield [a]	kg ha^{-1}	87.1	86.7

[a] The sugarcane yield is the cane stalk sent for processing.

The energy utilised by diesel consumption is calculated using parameters stated in Table 3.7. The data in Table 3.13 presented by both studies are based in Brazil. Both present a similar total fossil fuel consumption per ton of sugarcane, where the average is considered in this study: -139.11 MJ t_{cane}^{-1}.

3.2.4 First generation production of bioethanol

Initially, the sugarcane is cleaned to remove any soil and impurities (Furlan, Tonon Filho, *et al*, 2013). The sugarcane stalk is then milled using a sequence of crushing rollers to extract the saccharides from the cane. Water is added during imbibition for the last section of crushing rollers to increase the extraction efficiency (Dias, Junqueira, Cavalett, Pavanello, *et al*, 2013; Modesto, Zemp & Nebra, 2009). The juice extract is known as molasses (or raw juice). The bagasse is a byproduct from the milling step that is recovered with a moisture of 50 wt. %.

The molasses contains impurities (such as fibres and dirt) that are removed during pretreatment, prior to the fermentation step. The sugarcane juice is passed through hydrocyclones and screens to remove most of the dirt and fibres (Dias, Ensinas, *et al*, 2009).

Phosphoric acid is the added to the stream to promote better sedimentation of the impurities during clarification (Dias, Ensinas, *et al*, 2009). The molasses is then preheated to 70 °C, whereafter calcium oxide (CaO) is added to neutralise the solution (Dias, Ensinas, *et al*, 2009; Petersen, Van der Westhuizen, *et al*, 2018). The mixture is then heated up to 105 °C and de-aerated (Furlan, Tonon Filho, *et al*, 2013; Silva Ortiz, Maciel Filho & Posada, 2019).

The mixture is then clarified in a settler where mud and clarified juice exit the settler (Furlan, Tonon Filho, *et al*, 2013). It is assumed that the clarified juice contains only sucrose and glucose in solution, where all the remaining impurities (with some sugar) is contained in the mud. The mud is filtered to recover the sugars in the filtrate which is recycled (Dias, Ensinas, *et al*, 2009).

The clarified juice is then concentrated in a multi-effect evaporator to increase the sugar concentration (Furlan, Tonon Filho, *et al*, 2013). The final sucrose concentration is 22 wt. % (Dias, Ensinas, *et al*, 2009). The juice is then sterilised before fermentation where it is heated to 130 °C (Dias, Ensinas, *et al*, 2009).

The sterilised juice is then cooled and fed into a fermenter with recycled yeast (Dias, Ensinas, *et al*, 2009). In the reactor, sucrose is converted to glucose via hydrolysis according to Equation 3.1:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Glucose}}{2\,C_6H_{12}O_6} \tag{3.1}$$

The conversion of sucrose to glucose is assumed to be 100 mol %. This is a reasonable assumption intended to achieve a bioethanol yield comparable to reported literature values (Dias, Cunha, Jesus, Scandiffio, *et al*, 2010).

The resulting glucose is then fermented to ethanol according to Equation 3.2:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Ethanol}}{2\,C_2H_6O} + \underset{\text{Carbon dioxide}}{2\,CO_2} \tag{3.2}$$

In the fermenter, a portion of the glucose is converted to glycerol, succinic acid, acetic acid, isoamyl alcohol, and yeast. These products of glucose conversion are neglected from the mass and energy balances for simplicity. Furthermore, the co-products are removed during the ethanol purification step regardless and are therefore considered as waste products. As a result, this study only considers the conversion of glucose to ethanol with a mass yield of 90.48 % Dias, Cunha, Jesus, Scandiffio, *et al* (2010), Furlan, Costa, *et al* (2012), and Dias, Ensinas, *et al* (2009).

The ethanol-rich stream coming out of the fermenter is called wine. The CO_2 is removed from the wine through absorption where ethanol vapours are also recovered (Dias, Ensinas, *et al*, 2009). The wine is centrifuged to separate the yeast and the yeast is then treated and recycled to the fermenter (Dias, Ensinas, *et al*, 2009; Furlan, Tonon Filho, *et al*, 2013).

The wine is then distilled to obtain hydrous ethanol at a concentration of 93 wt. % ethanol (Dias, Junqueira, Cavalett, Pavanello, *et al*, 2013). The hydrous ethanol is then dehydrated to anhydrous ethanol with a concentration of to 99.6 wt. % using molecular sieves (Furlan, Tonon Filho, *et al*, 2013; Dias, Junqueira, Cavalett, Pavanello, *et al*, 2013). Dehydration using molecular sieves is preferred as it is a less energy intensive process compared to azeotropic distillation with cyclohexane (Cavalett *et al*, 2012). The overall recovery of ethanol for distillation and dehydration is taken as 99.7 wt. % (Dias, Cunha, Jesus, Scandiffio, *et al*, 2010). The impurities that are removed during ethanol purification are known as vinasse (Almeida & Colombo, 2021).

3.2.5 Second generation production of bioethanol

Methods of 2G bioethanol production

Lignocellulosic biomass consists of mainly cellulose, hemicellulose, lignin, and small amounts of extractives and ash (Carvalho *et al*, 2020; Kumar *et al*, 2021). Lignocellulose can be converted into ethanol via biochemical, thermochemical, or hybrid routes. The biochemical conversion is most established due to its similarities with first generation bioethanol production; this allows for lower cost infrastructure as the unit operations may be integrated between the 2G and 1G processes (Liguori *et al*, 2016). Biochemical conversion involves 3 steps: 1) pretreatment 2) saccharification/hydrolysis and 3) fermentation of sugars to ethanol (Michailos & Webb, 2019).

The biomass fibres are arranged in a complex network where the lignin and hemicellulose form a barrier surrounding the cellulose (Carvalho *et al*, 2020). Pretreatment is used to break up the lignocellulosic components, making cellulose more available for hydrolysis (Albuquerque Wanderley *et al*, 2013; Canettieri *et al*, 2007; Oliveira, Pinheiro, *et al*, 2013; Carvalho *et al*, 2020; Carrasco *et al*, 2010). Several pretreatment methods are shown in Figure 3.11.

Hydrolysis involves the breakdown of fibres, which are polysaccharides, into fermentable sugars (Velásquez-Arredondo, Ruiz-Colorado, *et al*, 2010; Wyman *et al*, 2005). The hydrolysis of cellulose can be accomplished through acidic or enzymatic catalysis. Enzymatic hydrolysis is the most widely used method due to the higher sugar yields, the lower cost of operation, and the minimisation of the inhibitory effects of lignin (Michailos & Webb, 2019).

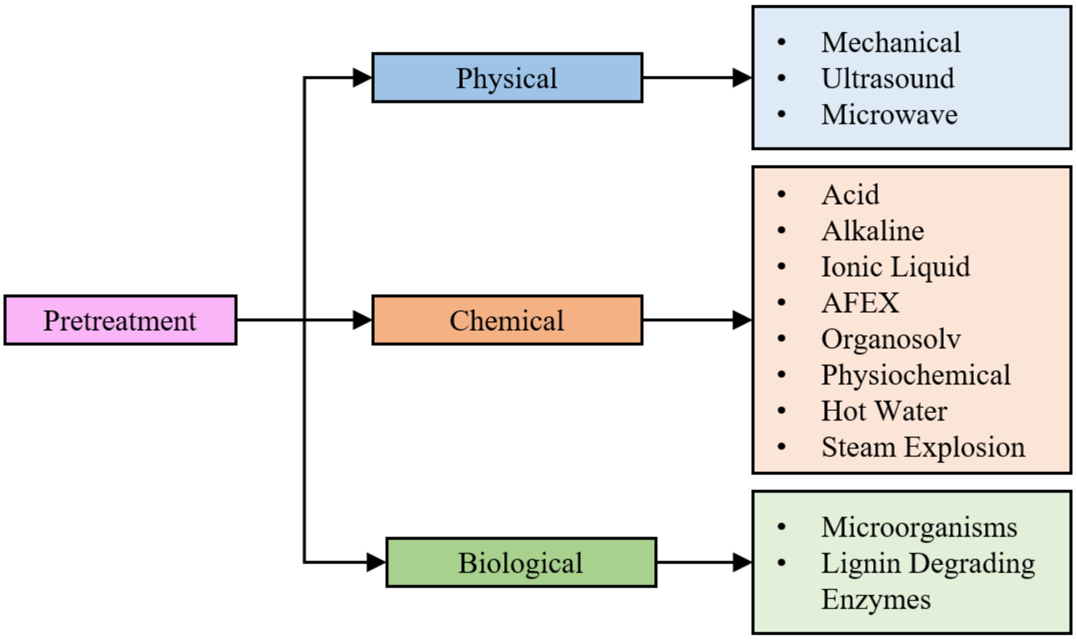


Figure 3.11: Methods of lignocellulose pretreatment. *The image has been adapted from Kumar, Kumar, Singh,* et al *(2021).*

The most predominant method of pretreatment is steam explosion. Steam explosion followed by enzymatic hydrolysis has been successfully implemented on small-scale plants (Ayodele *et al*, 2020) as well as in industrial scale plants in Brazil.

Steam explosion as a pretreatment method is advantageous for the following reasons (Rocha, Martín, *et al*, 2012; Ortiz & Oliveira Jr, 2014; Oliveira, Pinheiro, *et al*, 2013; Bezerra & Ragauskas, 2016; Soccol *et al*, 2010; Dias, Cunha, Maciel Filho, *et al*, 2011; Ayodele *et al*, 2020):

- It is highly effective at solubilising hemicellulose and increasing the cellulose-accessibility for hydrolysis.
- Steam explosion has a relatively low cost.
- It has a reduced environmental impact due to the low chemical consumption.
- It produces almost no inhibitory compounds for the fermentation of sugars.

For the reasons stated above, steam explosion followed by enzymatic hydrolysis is considered in this study.

The use of bagasse and straw for 2G bioethanol

Although bagasse and sugarcane straw are both lignocellulose, the residues have very different physical characteristics (Menandro *et al*, 2017). Subsequently, it is important to validate the hydrolysis yields of the residues depending on whether bagasse, straw, or a mixture is valorised in 2G production.

Pereira *et al* (2015) evaluated the use of the sugarcane straw, tops, and bagasse separately for 2G bioethanol using dilute acid pretreatment, eznymatic hydrolysis, and fermentation. The authors found that 2G ethanol production significantly improves when using the combination of straw and tops with the bagasse compared to the bagasse alone. Carvalho *et al* (2020) investigated the production of 2G bioethanol from the mixed residue of bagasse and straw in a pilot plant. The hydrolysis yields achieved were comparable to yields associated with only bagasse.

The 2G bioethanol model presented in this study is predominantly based on the models developed by Dias, Junqueira, Cavalett, Cunha, Jesus, Rossell, *et al* (2012) and Ortiz & Oliveira Jr (2014). The former investigated an integrated 1G and 2G bioethanol process using sugarcane bagasse and straw for the 2G production. The latter publication was an exergy analysis of bioethanol production from bagasse. It is assumed that the model parameters cited in this study sufficiently represent the associated yields obtainable for the 2G production of bagasse, straw, or a combination of both, regardless of the model scenario.

Process model for 2G bioethanol

The lignocellulosic material (bagasse and/or trash) is pretreated using saturated steam. The steam is injected into a reactor to achieve a pressure of 1.25 MPa and a temperature of 190 °C (Ortiz & Oliveira Jr, 2014; Rocha, Gonçalves, *et al*, 2012). This is followed by a rapid decompression where the steam dismantles the lignocellulosic fibres (Oliveira, Pinheiro, *et al*, 2013; Zhao *et al*, 2015).

During pretreatment, most of the hemicellulose hydrolyses to pentoses, mainly xylose ($C_5H_{10}O_5$), and a small amount of acetic acid ($C_2H_4O_2$), furfural ($C_5H_4O_2$) and glucose ($C_6H_{12}O_6$) are produced (Rocha, Gonçalves, *et al*, 2012; Dias, Junqueira, Cavalett, Cunha, Jesus, Rossell, *et al*, 2012; Ortiz & Oliveira Jr, 2014).

In terms of the hemicellulose hydrolysis, xylose is the desirable product as it is intended for fermentation to ethanol. The co-products (acetic acid, furfural, and glucose) would be removed during the distillation step and are therefore waste products. For simplicity, only the hydrolysis of hemicellulose to xylose is considered, according to Equation 3.3.

$$\underset{\text{Hemicellulose}}{C_5H_8O_4} + \underset{\text{Water}}{H_2O} \rightarrow \underset{\text{Xylose}}{C_5H_{10}O_5} \tag{3.3}$$

The liquid fraction (hemicellulose hydrolysate) is separated from the solid fraction using filters. The solid fraction consists of mainly cellulose and lignin (cellulignin) (Oliveira, Pinheiro, *et al*, 2013). The xylose in the liquid fraction can be fermented to ethanol using yeast *Pichia stipitis* or biodigested to produce biogas—the biogas can then be used in cogeneration (Carrasco *et al*, 2010; Dias, Modesto, *et al*, 2011; Petersen, Aneke & Görgens, 2014). This study considers the fermentation of the pentose sugars to maximise the ethanol yield. The C_5 fermentation reaction is shown in Equation 3.4.

$$\underset{\text{Xylose}}{3\,C_5H_{10}O_5} \rightarrow \underset{\text{Ethanol}}{5\,C_2H_6O} + \underset{\text{Carbon Dioxide}}{5\,CO_2} \tag{3.4}$$

The xylose-fermentation yield considered by Dias, Junqueira, Cavalett, Cunha, Jesus, Rossell, *et al* (2012) is 80 %. Although the technology is not mature, the authors cite that values as high as 95 % have been achieved in lab and pilot scale studies. However, a more conservative estimate was used by the authors due to the inhibition of contaminants and low productivity of the microorganisms on an industrial scale. After fermentation, the ethanol produced from xylose is then mixed with the wine from the 1G process which is then sent to the 1G distillation and dehydration operations.

The cellulosic pulp is then sent for enzymatic hydrolysis. Generally, about 70 % of the cellulose and residual hemicellulose is hydrolysed to glucose (Dias, Junqueira, Cavalett, Cunha, Jesus, Rossell, *et al*, 2012). The hydrolysis of cellulose is shown in Equation 3.5.

$$\underset{\text{Cellulose}}{C_6H_{10}O_5} + \underset{\text{Water}}{H_2O} \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} \tag{3.5}$$

The glucose-rich liquor is then separated from the residual cellulignin (solid fraction). The glucose liquor is mixed with the clarified juice in the 1G process and then fermented to ethanol. The fermentation yield of the glucose from the 2G process is assumed to be the same as the 1G glucose-conversion process already described.

The unreacted solids in the cellulignin stream are then sent to cogeneration. This allows for the recovery of the energy dense compounds for the generation of excess electricity.

It should be noted that alkaline delignification may be performed prior to the hydrolysis of cellulose. Lignin is known to have an inhibitory effect on the enzymes present during the hydrolysis and fermentation processes (Phuttaro *et al*, 2019; Zhao *et al*, 2015). To mitigate this issue, alkaline delignification using dilute NaOH can be performed to solubilise most of lignin and increase the accessibility of the cellulose for hydrolysis (Rocha, Martín, *et al*, 2012; Dias, Cunha, Maciel Filho, *et al*, 2011; Dias, Junqueira, Rossell, *et al*, 2013). The lignin may also be precipitated out of solution using an acid where it can then be sent to cogeneration (Dias, Junqueira, Rossell, *et al*, 2013).

Alkaline deliginification is not considered in this study. Lignin precipitation is an involved process with various unit operations. Furthermore, the cellulignin stream is sent to cogeneration regardless which contains the lignin and residual cellulose.

3.3 The cogeneration model

Conventional cogeneration systems employ a steam-based Rankine cycle. Superheated steam is produced by a boiler and is expanded in back-pressure steam turbines to supply the biofuel process with process steam and electricity (Camargo *et al*, 2020). This configuration generates live steam that is determined by the process steam demands (Ensinas *et al*, 2007). Alternatively, when a surplus of electricity is desired, a condensing steam turbine is introduced. Excess live steam can be produced by the boiler and expanded to below atmospheric pressure, which improves the conversion of enthalpy of the superheated steam (De Pretto *et al*, 2017).

The thermal efficiencies of cogeneration systems are largely dependent on the steam condition produced by the boiler. Traditional boilers in cogeneration systems raise the steam to low pressure and temperature (20 bar and 350 °C) resulting in low energy efficiency (Dias, Modesto, *et al*, 2011; Ensinas *et al*, 2007). The generation of surplus electricity to be sold to the grid has become of greater importance, especially in the context of increasing energy renewability (Dias, Modesto, *et al*, 2011). Consequently, more efficient cogeneration systems have become adopted where boilers produce superheated steam at higher pressures and temperatures (65 bar and 510 °C, 90 bar and 520 °C, and 100 bar and 530 °C) (Castineiras Filho & Pradelle, 2020; Carpio & Souza, 2017; Walter & Ensinas, 2010; Dias, Junqueira, Cavalett, Cunha, Jesus, Rossell, *et al*, 2012). In the case of an integrated first and second generation bioethanol plant, higher pressure boilers consume more lignocellose (namely bagasse) compared to low pressure boilers, for the production of process steam. As a consequence, less bagasse can be diverted to bioethanol production. The larger generation of electricity using high pressure boilers does favour the economic feasibility of bioethanol plants (Dias, Junqueira, Cavalett, Cunha, Jesus, Mantelatto, *et al*, 2013). For this study, a high pressure boiler (90 bar) is considered for this reason.

3.3.1 Cogeneration for the soybean-biodiesel process

The following discussion relates to the cogeneration system for the biodiesel production plant. The specifications of the streams in the Rankine cycle are shown in Figure 3.12. Depending on the scenario of the simulation, the boiler utilises the by-products (trash, hulls, meal, or glycerol) and/or fossil fuels to generate steam at 90 bar and 520 °C. The steam from the boiler (m_1) is expanded in a back-pressure steam turbine (Turbine 1) to the pressure of the process steam (P_3) and electricity is produced. A portion of this steam is used for the process (m_3). Surplus steam that is not required by the process (m_4) is sent to the condensing steam turbine (Turbine 2) which generates excess electricity. The outlet of Turbine 2 is at 0.085 bar (Ensinas *et al*, 2007; De Pretto *et al*, 2017); well below atmospheric pressure in order to maximise the electrical energy output. The expanded steam is sent to a condenser, and a pump (Pump 2) raises the pressure of the condensate to atmospheric pressure (1.01 bar) for the boiler to receive it.

According to Sheehan *et al* (1998), the unit operations of the biodiesel process utilise saturated steam at 10.3 bar (at and equivalent temperature of 181 °C). These are the conditions of Stream 3c. The steam is returned from the process as a condensate at 1.01 bar (Stream 8). However, the outlet of Turbine 1 is a superheated vapour. Furthermore, Stream 7a is a subcooled liquid. A heat exchanger is included for heat recovery—the temperature of Stream 7a is raised and the temperature of Stream 3a is decreased. The minimum temperature allowed for Stream 3b is the saturation temperature of the vapour and the maximum temperature allowed for Stream 7b is the saturation temperature of the liquid. The subsequent calculations explain the relevant logic. A cooler is intended to ensure that Stream 3 enters the process as a saturated vapour after the heat exchange. Stream 9 is the product of mixing Stream 8 from the process and Stream 7c from the heat exchanger. Pump 1, increases the pressure to the operating pressure of the boiler (90 bar).

Depending on the scenario, the amount of available energy from the by-products sent to the boiler varies. Consequently, the mass of steam sent to the condensing steam turbine

(m_4) will vary. The mass balance is performed to first meet the steam requirements of the process (m_3) and any excess steam is used to generate surplus electricity in Turbine 2.

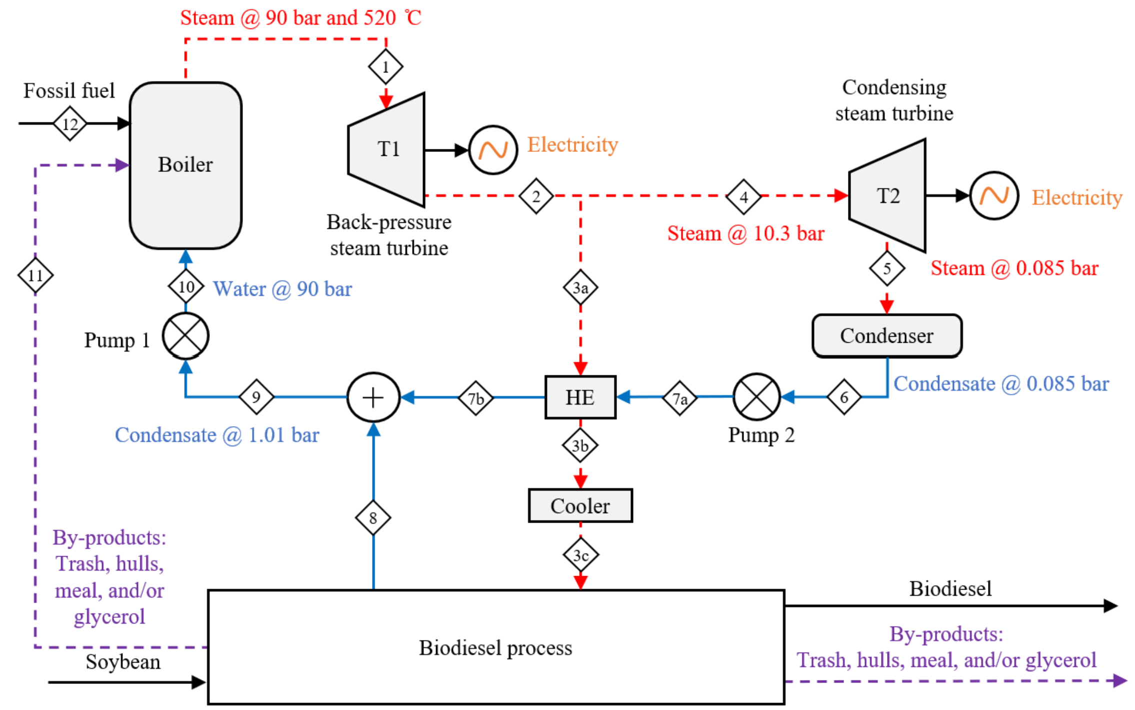


Figure 3.12: Cogeneration for the biodiesel processing plant based on the Rankine Cycle.

Table 3.14 describes the relevant efficiencies to model the cogeneration system.

Table 3.14: Cogeneration process parameters.

Parameter	Symbol	Value
Boiler efficiency [a]	η_{boiler}	87 %
Pump isentropic efficiency [b, c]	η_{pump}	80 %
Turbine isentropic efficiency [b, c, d]	η_{turbine}	80 %
Electric generator efficiency [a, d]	$\eta_{\text{generator}}$	98 %

[a] Dias, Junqueira, Cavalett, Cunha, Jesus, Rossell, *et al* (2012)

[b] De Pretto, Tardioli & Costa (2017)

[c] Ensinas *et al* (2007)

[d] Dias, Modesto, *et al* (2011)

The following calculations were performed using procedures detailed in Smith (1950). The applicable thermodynamic properties of the streams were calculated using CoolProp (Bell *et al*, 2014) in Python (Van Rossum & Drake, 2009).

First, the work produced by Turbine 1 is calculated; Stream 1 is fully specified. The ideal work of Turbine 1 is determined assuming a reversible and adiabatic operation, where the entropy of Stream 2 is equal to that of Stream 1 ($s_{2'} = s_1$):

$$W_{\text{T1 ideal}} = h_{2'} - h_1 \tag{3.6}$$

The real work produced by Turbine 1 is then determined from the isentropic efficiency:

$$W_{\text{T1 real}} = W_{\text{T1 ideal}}(\eta_{\text{turbine}}) \tag{3.7}$$

The real enthalpy (and subsequent properties) of Stream 2 are then calculated:

$$h_2 = W_{\text{T1 real}} + h_1 \tag{3.8}$$

The real work of Turbine 2 and the isentropic and real conditions of Stream 5 can be determined analogously. The properties of Stream 6 are also fully specified. The enthalpy of Stream 7a is determined assuming reversible and adiabatic pump operation where the entropy of Stream 7a is equal to that of Stream 6 ($s_{7a'} = s_6$). The condensate is assumed to be incompressible.

$$h_{7a'} = \left(\frac{1}{\rho_6}\right)(P_{7a} - P_6) + h_6 \tag{3.9}$$

The ideal work of Pump 2 is then calculated:

$$W_{\text{P2 ideal}} = h_{7as} - h_6 \tag{3.10}$$

The real work of Pump 2 is determined from the isentropic efficiency:

$$W_{\text{P2 real}} = \frac{W_{\text{P2 ideal}}}{\eta_{\text{pump}}} \tag{3.11}$$

The real enthalpy of Stream 7a is then determined:

$$h_{7a} = W_{\text{P2 real}} + h_6 \tag{3.12}$$

As already discussed, the process utilises saturated steam from Stream 3 and the steam is consumed and returned as a condensate. However, the steam from Turbine 1 is superheated. Furthermore, Stream 7a is subcooled. A heat exchanger is modelled in order raise the temperature of Stream 7a to saturation temperature (at maximum) and to reduce the temperature of Stream 3a to saturation temperature (at minimum). A simple set of equations from Çengel & Ghajar (2020: 659) is used to model the heat exchange.

The heat exchanger is assumed to be perfectly insulated where the heat transfer only occurs between the hot and cold fluids. Subsequently, the rate of heat transfer, $\dot{Q}$, is given by Equation 3.13 or Equation 3.14 in J s^{-1}:

$$\dot{Q} = mc_{p,h}(T_{h,\text{in}} - T_{h,\text{out}}) \tag{3.13}$$

$$\dot{Q} = mc_{p,c}(T_{c,\text{out}} - T_{c,\text{in}}) \tag{3.14}$$

where c_p is the specific heat of the fluid. The subscripts c and h indicate the cold and hot streams respectively, which correspond to Stream 7 and Stream 3 respectively. It should be noted that the cogeneration model has been coded in Python to fulfill all scenarios. For a heat exchange, the temperature of the cold stream may never exceed that of the hot stream. These thermodynamic principles are respected in the model by considering the heat capacity rate of the hot and cold streams (C_h and C_c). The heat capacity rate is the product of the mass flow rate and the specific heat of the fluid:

$$C_h = m_h c_{p,h} \tag{3.15}$$

$$C_c = m_c c_{p,c} \tag{3.16}$$

The fluid having the larger heat capacity rate undergoes a smaller temperature change and vice versa. For a given mass flowrate of Stream 7 and Stream 3, the heat capacity rates were calculated and compared. If $C_3 > C_7$, then Stream 7 experiences a larger temperature change. As a result, the temperature of Stream 7b is specified at the saturation temperature of liquid water and the temperature of Stream 3b is calculated. Conversely, if $C_3 < C_7$, then the temperature of Stream 3b is set to the saturation temperature of the vapour and the temperature of Stream 7b is calculated. This was done to ensure that Stream 7 is at the saturated temperature or lower and Stream 3b is at the saturation temperature of vapour (or higher).

The enthalpies of Stream 7b and Stream 3b can then be calculated:

$$h_{7b} = \frac{m_7 h_{7a} + \dot{Q}}{m_7} \tag{3.17}$$

$$h_{3b} = \frac{m_3 h_{3a} - \dot{Q}}{m_3} \tag{3.18}$$

Finally, if Stream 3b is still a superheated vapour after the heat exchange, then a cooler is used to reduce the temperature of Stream 3c to a saturated vapour. This ensures the the change in enthalpy of the process steam is modelled correctly. Stream 3c is therefore fully specified as a saturated vapour at 10.3 bar.

The utility of the process steam, $\Delta H_{\text{process steam}}$, is therefore calculated based on the enthalpy of Stream 3c and Stream 8:

$$\Delta H_{\text{process steam}} = h_{3c} - h_8 \tag{3.19}$$

The energy balance surrounding mixing Stream 7b and Stream 8 is calculated to determine the enthalpy and subsequent properties of Stream 9:

$$h_9 = \frac{m_7 h_{7b} + m_8 h_8}{m_9} \tag{3.20}$$

where $m_8 = m_3$ and $m_9 = m_7 + m_8$

The real work required by Pump 1 and the real enthalpy and subsequent properties of Stream 10 are determined analogously to that of Pump 2 and Stream 5.

The heat required by the boiler is given by:

$$Q_{\text{boiler}} = h_1 - h_{10} \tag{3.21}$$

It should be noted that an iterative procedure is needed in order to satisfy the complete mass and energy balance of the cogeneration system. Although the boiler heat requirement is given by Equation 3.21, it is also determined by considering the energy available from the boiler feedstock:

$$Q_{\text{boiler}} = \frac{(m_{11}\text{LHV}_{11} + m_{12}\text{LHV}_{12})\eta_{\text{boiler}}}{m_{10}} \tag{3.22}$$

The value of Q_{boiler} then determines how much excess steam (m_4) is sent to the condensing steam turbine. The mass flowrate out of the condenser (m_{7a}) and the subsequent heat exchange with Steam 3a affects the final enthalpy of Stream 10. This in turn affects the value of Q_{boiler}. Therefore, for each relevant scenario, Q_{boiler} was solved for iteratively depending on the amount of by-products burnt in the boiler for steam generation.

Finally, the total electrical energy generated, $E_{\text{generated}}$, is given by:

$$E_{\text{generated}} = (m_1 W_{\text{T1 real}} + m_4 W_{\text{T2 real}})\eta_{\text{generator}} - (m_9 W_{\text{P1 real}} + m_6 W_{\text{P2 real}}) \tag{3.23}$$

The surplus electricity generated, E_{surplus}, for the biorefinery is then calculated:

$$E_{\text{surplus}} = E_{\text{generated}} - E_{\text{elec. cons.}} \tag{3.24}$$

where $E_{\text{elec. cons.}}$ is the electrical energy consumed by the biorefinery process operations.

The above calculations were utilised in the defined scenarios to determine the overall energy balance of the plant.

Table 3.15: Results of the cogeneration model for soybean-biodiesel.

Parameter	Value
Q_{boiler}*	-3.007 MJ $\text{kg}_{\text{steam}}^{-1}$
$\Delta H_{\text{process steam}}$	-2.359 MJ $\text{kg}_{\text{steam}}^{-1}$
$W_{\text{T1 real}}$	-0.4708 MJ $\text{kg}_{\text{steam}}^{-1}$
$W_{\text{T2 real}}$	-0.6266 MJ $\text{kg}_{\text{steam}}^{-1}$
$W_{\text{P1 real}}$	-0.01161 MJ $\text{kg}_{\text{water}}^{-1}$
$W_{\text{P2 real}}$	-0.000117 MJ $\text{kg}_{\text{water}}^{-1}$
Trash LHV_{AR}	-14.78 MJ kg^{-1}
Hull LHV_{AR}	-10.93 MJ kg^{-1}
Meal LHV_{AR}	-11.54 MJ kg^{-1}
Glycerol LHV_{AR}	-11.64 MJ kg^{-1}

*This value is for Scenario 2.1 but will vary depending on the scenario

3.3.2 Cogeneration for the sugarcane-bioethanol process

Tha Rankine cycle applicable to the bioethanol refinery is shown in Figure 3.13. The boiler is fed with waste- and by-products from the process (sugarcane straw, bagasse, and cellulignin) and/or fossil fuels, depending on the process scenario.

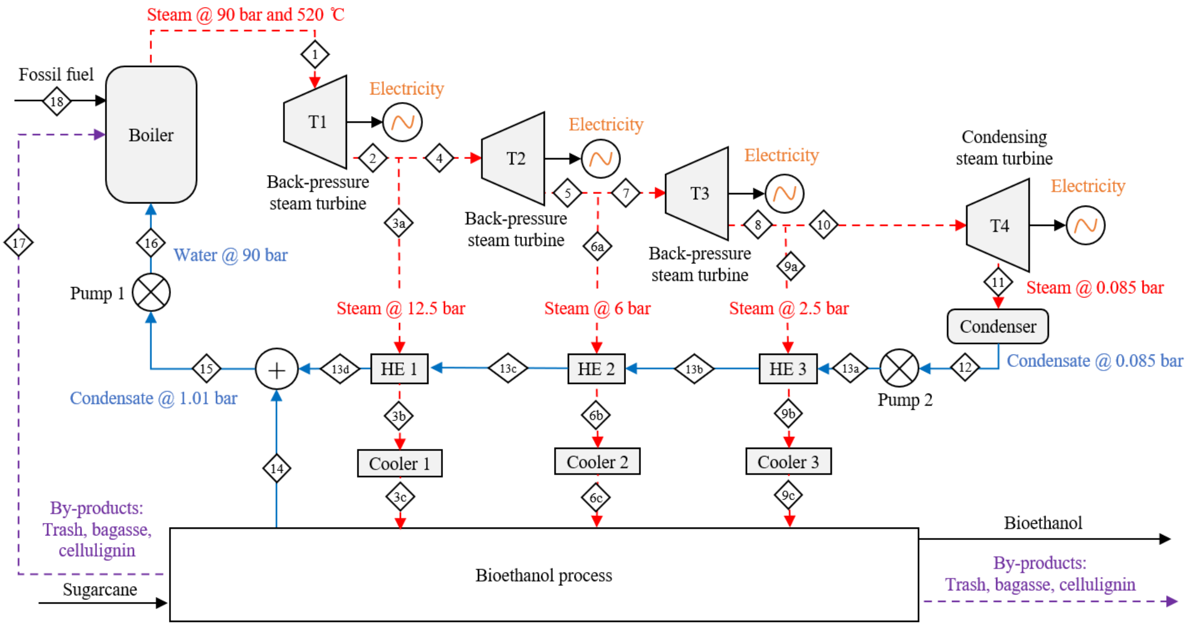


Figure 3.13: Cogeneration for the bioethanol processing plant based on the Rankine Cycle.

The boiler produces steam at 90 bar and 520 °C. Steam is expanded in three back-pressure steam turbines to supply the process with saturated steam: 12.5 bar from Turbine 1, 6 bar from Turbine 2, and 2.5 bar from Turbine 3. The 1G process utilises saturated steam at 6 bar and 2.5 bar. Only the 2G process requires saturated steam at 12.5 bar. The steam required for the unit operations in the bioethanol production process are shown in Appendix B. Therefore, if the scenario simulated does not include the 2G process, Turbine 1 is omitted from the model. Surplus steam is sent to the condensing steam turbine (Turbine 4) to produce surplus electricity.

The parameters of the model are taken from Table 3.14. The underlying calculations of the cogeneration model for the sugarcane-bioethanol process are not repeated because the calculations and logic thereof are analogous to Section 3.3.1. The calculated parameters for the model are shown in Table 3.16:

Table 3.16: Results of the cogeneration model for sugarcane-bioethanol.

Parameter	Value
Q_{boiler}^{*}	-3.007 MJ $\text{kg}_{\text{steam}}^{-1}$
$\Delta H_{\text{process steam}}$ at 12.5 bar	-2.366 MJ $\text{kg}_{\text{steam}}^{-1}$
$\Delta H_{\text{process steam}}$ at 6 bar	-2.337 MJ $\text{kg}_{\text{steam}}^{-1}$
$\Delta H_{\text{process steam}}$ at 2.5 bar	-2.297 MJ $\text{kg}_{\text{steam}}^{-1}$
$W_{\text{T1 real}}$	-0.4382 MJ $\text{kg}_{\text{steam}}^{-1}$
$W_{\text{T2 real}}$	-0.1327 MJ $\text{kg}_{\text{steam}}^{-1}$
$W_{\text{T3 real}}$	-0.1363 MJ $\text{kg}_{\text{steam}}^{-1}$
$W_{\text{T4 real}}$	-0.4044 MJ $\text{kg}_{\text{steam}}^{-1}$
$W_{\text{P1 real}}$	-0.01161 MJ $\text{kg}_{\text{water}}^{-1}$
$W_{\text{P2 real}}$	-0.00012 MJ $\text{kg}_{\text{water}}^{-1}$
Trash LHV_{AR}	-13.61 MJ kg^{-1}
Bagasse LHV_{AR}	-7.218 MJ kg^{-1}
Cellulignin LHV_{AR}	-17.44 MJ kg^{-1}

*This value is for Scenario 2.2 but will vary depending on the scenario

3.3.3 Conversion of the biomass feedstock to electricity

The conversion of the entire biomass crop (sugarcane or soybean) to electrical energy is modelled after a simple Rankine cycle as shown in Figure 3.14:

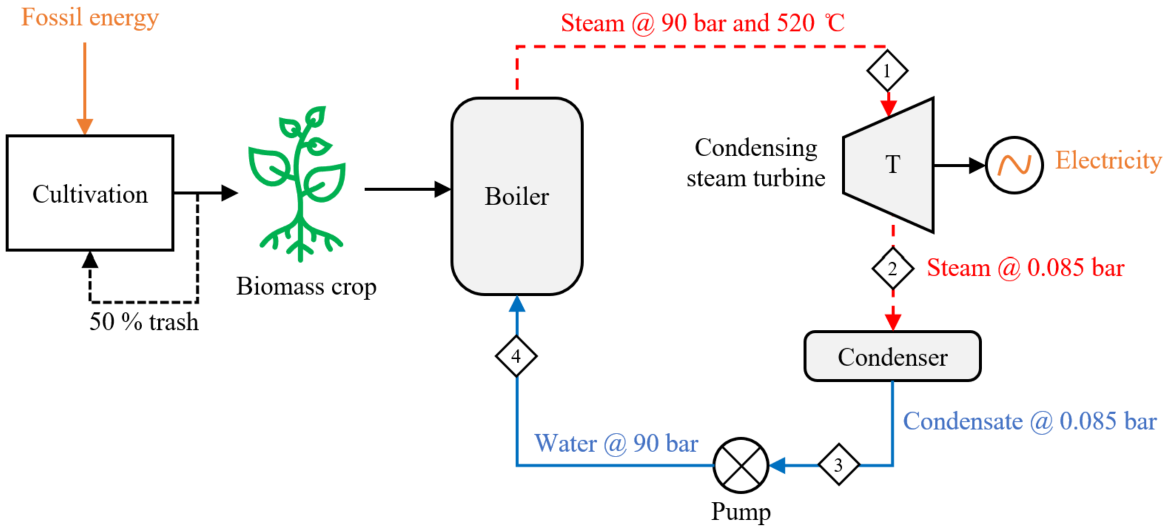


Figure 3.14: Rankine cycle for the conversion of biomass crop to electrical energy.

The steam conditions evolved from the boiler and condensing steam turbine is identical to the above cogeneration models. The condenser produces saturated water at 0.085 bar and a pump increases the water pressure to 90 bar. The conversion of the biomass crop to electricity is calculated similarly to the cogeneration model in the previous subsections. The same turbine, pump, and boiler efficiencies are used from Table 3.14. The results for the Rankine cycle model are shown in Table 3.17:

Table 3.17: Results for Rankine cycle for the direct conversion of biomass feedstock to electricity.

Parameter	Value
Q_{boiler}	-3.248 MJ $\text{kg}_{\text{steam}}{}^{-1}$
$W_{\text{T real}}$	-1.062 MJ $\text{kg}_{\text{steam}}{}^{-1}$
$W_{\text{P real}}$	-0.01134 MJ $\text{kg}_{\text{steam}}{}^{-1}$
Sugarcane Trash LHV_{AR}	-13.61 MJ kg^{-1}
Sugarcane LHV_{AR}	-2.421 MJ kg^{-1}
Soybean Trash LHV_{AR}	-14.78 MJ kg^{-1}
Soybean LHV_{AR}	-14.96 MJ kg^{-1}

3.4 The tank-to wheel cycle

After converting the biomass plant to the biofuel, the conversion of the fuel to mechanical energy in an internal-combustion engine (ICE) is modelled. This is known as the tank-to-wheel (TTW) cycle. The TTW phase measures energy consumed to supply a vehicle with energy via a pump/electric charging station to complete a driving cycle (Brito *et al*, 2013). For electric vehicles, stored electric energy is lost during the transfer of electrical energy from the charging station to the car-battery. However, for ICEs, the conservation of liquid fuels is considered to be 100 % where practically no liquid fuel losses occur.

During fuel combustion in the engine, the efficiency of converting the liquid fuel to useful mechanical energy depends on the type of engine (spark ignition for gasoline *vs.* compression ignition for diesel) and the region of the engine map at which the vehicle is operated (Brito *et al*, 2013). However, it is well established that ICEs on average only convert about 12 %–25 % of the available liquid fuel energy to useful mechanical work (Williamson, Lukic & Emadi, 2006; Leach *et al*, 2020). The upper efficiency limit of 25 % is assumed for the TTW phase, regardless of the fuel type (biodiesel *vs.* gasoline). The TTW efficiency describes that for every 100 MJ of fuel consumed by a vehicle, 25 MJ is converted into mechanical work.

Chapter 4: Methods

4.1 The system boundary

The system boundary considered in this study is shown below:

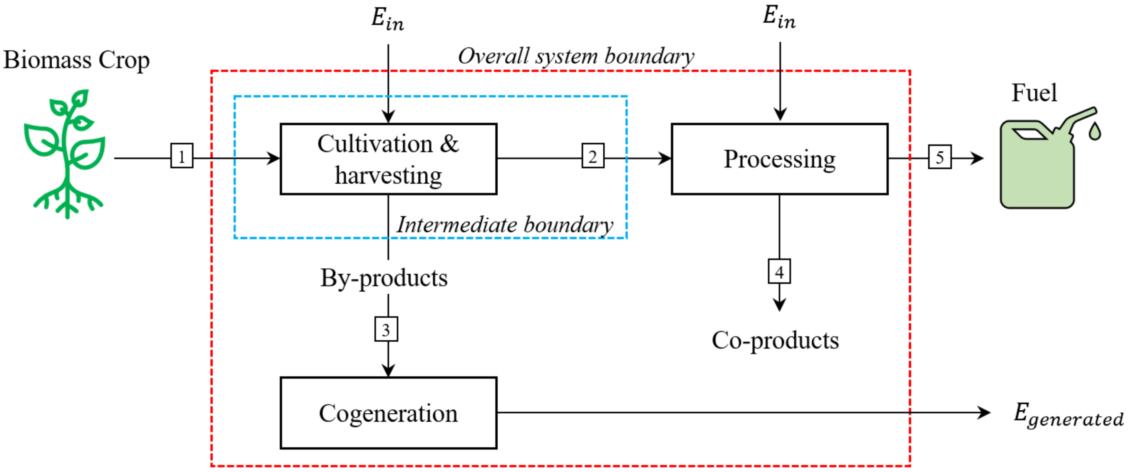


Figure 4.1: The system boundary used for this study. *The example intermediate boundary is included to illustrate the application of the energy metrics on a cumulative basis.*

The system boundary is intended to take into account *processing operations*. This is to place a focus on process efficiency rather than "life-cycle efficiency". When the boundary is extended to take into account transportation and other activities, the cross-field comparisons among biofuels becomes convoluted.

The system boundary considers the following:

- The input into the process is the entire cultivated crop. This reference state is chosen so as to embody the entire process cycle of the parent biomass.
- The energy inputs, E_{in}, considers all material and fuel inputs with an inherent higher heating value (such as diesel, natural gas, petroleum, hexane, methane etc.) and all energy utilities (such as steam and electricity). The energy consumption of the material/fuel inputs is calculated from the product of the mass flowrate and the HHV of the input. Therefore, material inputs with no calorific value are not taken into account for the energy consumption of the process.

- The system boundary is only concerned with processing operations. For this reason, the transportation of raw and intermediate products between different refineries are not considered. The only "transport energy" taken into account is for field-operations (such as diesel consumed for harvesters) as these are seen to be part of processing the biomass.

- Allocation methods are not applied. The by- and co-products are investigated in terms of their potential to improve the energy metrics; either through conversion to biofuels or to produce process heat and electricity.

4.2 Higher and lower heating values

The change in energy quality and the change in energy yield are calculated based on the energy carrying components on a dry and ash free (daf). Consequently, the energy carrying components on a daf are the components of interest for the subsequent energy metrics. Conventionally, the lower heating value (LHV) is calculated from the higher heating value (HHV) on a dry basis and considers the energy consumed to evaporate the water resulting from the combustion of fuel-bound hydrogen. The foundations of the paper rely on the strong correlation between $\Delta_c h^{\circ}{}_{\mathrm{HHV}}$ and the mass of oxygen combusted per mass of the fuel, $m_{\mathrm{O_2}}$, as described by Equation 2.3. The equation may be rewritten in terms of the elemental composition of the fuel, according to Equation 4.1 (Merckel, Labuschagne, *et al*, 2020):

$$\Delta_c h^{\circ}{}_{\mathrm{HHV}} = -13.87(n_{\mathrm{vC}} + \frac{1}{4}n_{\mathrm{vH}} - \frac{1}{2}n_{\mathrm{vO}} + n_{\mathrm{vS}} + \frac{5}{4}n_{\mathrm{vP}})\frac{M_{\mathrm{O_2}}}{M_{\mathrm{fuel}}} \tag{4.1}$$

where n_{vC}, n_{vH}, n_{vO}, n_{vS}, and n_{vP} are the moles of carbon, hydrogen, oxygen, sulphur, and phosphorus in the fuel, and $M_{\mathrm{O_2}}$ and M_{fuel} are the molar masses of oxygen and the fuel consumed during combustion respectively.

Equation 4.1 is employed to calculate $\Delta_c h^{\circ}{}_{\mathrm{HHV}}$ of the streams in the mass and energy balances and consequently, the energy metrics. However, when considering the actual energy evolved during a combustion process, the LHV, on an "as received basis" (AR), is more relevant. The LHV is calculated from the HHV by:

$$\mathrm{LHV_{daf}} = \mathrm{HHV_{daf}} - \Delta\mathrm{H_{vap}}\left(\frac{m_{\mathrm{H_2O}}}{m_{\mathrm{fuel}}}\right) \tag{4.2}$$

where $\Delta\mathrm{H}_{\mathrm{vap}}$ is the heat of vaporisation of water given as -2256.4 kJ kg^{-1}, $m_{\mathrm{H_2O}}$ is the mass of water produced during combustion of the dry fuel, and m_{fuel} is the mass of the fuel on a dry and ash free basis. The $\mathrm{LHV}_{\mathrm{AR}}$ is then calculated:

$$\mathrm{LHV}_{\mathrm{AR}} = \frac{\mathrm{LHV}_{\mathrm{daf}}(m_{\mathrm{fuel}}) - \Delta\mathrm{H}_{\mathrm{vap}}(m_{\mathrm{moisture}})}{m_{\mathrm{fuel}_{\mathrm{AR}}}} \tag{4.3}$$

where m_{moisture} is the mass of moisture in the material stream and $m_{\mathrm{fuel}_{\mathrm{AR}}}$ is the mass of the fuel on an as received basis.

The $\mathrm{LHV}_{\mathrm{AR}}$ takes into account the energy consumed to evaporate the moisture in the fuel per total unit mass of the fuel (including the mass of moisture and ash-forming minerals). Therefore, the moisture and ash is only considered for the purpose of determining the $\mathrm{LHV}_{\mathrm{AR}}$ of a material stream when appropriate—namely, when determining the quantity of energy evolved per unit mass of fuel during combustion with respect to a boiler.

4.3 The application of the change in energy quality

The change in energy quality, ΔE_{Q}, is applied to the system boundary according to Equation 2.4. For the biomass-to-biofuel processes, ΔE_{Q} is applied on a cumulative basis and on an overall basis. Evaluating the processing operations on a cumulative basis allows for the assessment of each unit operation.

ΔE_{Q} evaluates if the energy density of the fuel has been increased relative to the feedstock. Consequently, ΔE_{Q} only considers the material that contributes to the production of the biofuel. When applying the metric on a cumulative basis, the co-products and by-products are only taken into account if they are utilised for biofuel production. Furthermore, the energy consumed by the process is also not considered in ΔE_{Q}. For the example system boundary in Figure 4.1, the co-products are recovered as value-added products (not biofuels) and the by-products are used to generate process energy (heat and electricity). Therefore, ΔE_{Q} is computed for the intermediate boundary as

$$\Delta E_{\mathrm{Q}} = \frac{\Delta_c h^\circ|_{\mathrm{HHV,2}} - \Delta_c h^\circ|_{\mathrm{HHV,1}}}{\Delta_c h^\circ|_{\mathrm{HHV,1}}}$$

and for the overall process:

$$\Delta E_{\mathrm{Q}} = \frac{\Delta_c h^\circ|_{\mathrm{HHV,5}} - \Delta_c h^\circ|_{\mathrm{HHV,1}}}{\Delta_c h^\circ|_{\mathrm{HHV,1}}}$$

4.4 The application of the change in energy yield

ΔE_η, accounts for all streams that contribute to the energy recovered in the biofuel as well as for process energy. ΔE_η also considers the additional utility requirements, E_{in}, per unit of feedstock-derived energy, ΔE_{f}. In this way, ΔE_η considers the "net energy produced" during the process in relation to the biomass input.

The net energy consumed, $E_{cons.}$, is taken into account in Equation 2.6:

$$\Delta E_\eta = \frac{\Delta E_{\text{p}}}{\Delta E_{\text{f}}} - \frac{\Delta E_{\text{cons.}}}{\Delta E_{\text{f}}}$$

$$\Delta E_\eta = \frac{m_{\text{p}}\left(\Delta_c h^\circ|_{\text{HHV,p}}\right)}{m_{\text{f}}\left(\Delta_c h^\circ|_{\text{HHV,f}}\right)} - \frac{\Delta E_{\text{cons.}}}{m_{\text{f}}\left(\Delta_c h^\circ|_{\text{HHV,f}}\right)}$$

$$\Delta E_\eta = \eta\left(\frac{\Delta_c h^\circ|_{\text{HHV,p}} - \Delta E_{\text{cons.}}/m_{\text{p}}}{\Delta_c h^\circ|_{\text{HHV,f}}}\right) \tag{4.4}$$

where $\Delta E_{\text{cons.}}/m_{\text{p}}$ describes the net energy consumed per quantity of biofuel produced. It is important to note that the energy yield is normalized to the energy of the biomass into the process.

To illustrate the application of Equation 4.4, ΔE_η is defined for the intermediate boundary of Figure 4.1:

$$\Delta E_\eta = \frac{m_2 + m_3}{m_1}\left(\frac{\Delta_c h^\circ|_{\text{HHV,2-3}} - \Delta E_{\text{cons.}}/m_1}{\Delta_c h^\circ|_{\text{HHV,1}}}\right)$$

where $\Delta_c h^\circ|_{\text{HHV,2-3}}$ is the higher heating value of stream 2 and 3 combined. ΔE_η is written for the overall boundary as:

$$\Delta E_\eta = \frac{m_5}{m_1}\left(\frac{\Delta_c h^\circ|_{\text{HHV,5}} - \Delta E_{\text{cons.}}/m_1}{\Delta_c h^\circ|_{\text{HHV,1}}}\right)$$

4.5 The fossil energy ratio and net energy ratio

The fossil energy ratio (FER) and the net energy ratio (NER) for the biofuel production processes are also determined as a point of reference for the aforementioned energy metrics. The FER and NER are by no means the focus of this study. Rather, they provide insight into the current state of energy-analysis for biofuel production studies, against which the ΔE_{Q} and ΔE_{η} may be compared.

Allocation methods are not applied for the calculation of these metrics. It would be inconsistent to apply mass or energy allocation for the FER and the NER and not the ΔE_{Q} and ΔE_{η}.

The definition for the NER and FER were modified from Castineiras Filho & Pradelle (2020). The FER is given by Equation 4.5:

$$\mathrm{FER} = \frac{E_{\mathrm{surplus}} + (m_p)\Delta_c h^{\circ}|_{\mathrm{HHV,p}}}{E_{\mathrm{fossil}}} \tag{4.5}$$

where E_{surplus} is the energy of the surplus electricity produced, E_{fossil} is the fossil-derived energy consumed, and m_p is the mass of the biofuel, or product. Equation 4.5 therefore describes the total energy produced in the form of electricity and the biofuel relative to the fossil fuel energy consumed.

The NER, given by Equation 4.6, is similar to the FER. However, energy derived from renewable biomass (namely during cogeneration) is taken into account in the denominator:

$$\mathrm{NER} = \frac{E_{\mathrm{surplus}} + (m_p)\Delta_c h^{\circ}|_{\mathrm{HHV,p}}}{E_{\mathrm{fossil}} + (m_{\mathrm{biomass}})\Delta_c h^{\circ}|_{\mathrm{HHV,biomass}}} \tag{4.6}$$

where m_{biomass} and $\Delta_c h^{\circ}|_{\mathrm{HHV,biomass}}$ are the mass and higher heating value of biomass respectively. The biomass considered in Equation 4.6 refers only to biomass utilised for process steam and electricity. It does not refer to the feedstock crop which is the input into the process. This is inline with the way in which the NER is applied in life-cycle assessment studies.

4.6 Scenario definition

4.6.1 Biodiesel scenarios

Four groups of scenarios are modelled to for the soybean-biodiesel (SBD) process (see Figure 4.2):

- Scenario 1 is the ideal valorisation of the entire soybean crop. Scenario 1 is a theoretical maximum against which the real-life scenarios may be compared. The ideal valorisation considers the valorisation of the entire soybean crop including all trash that is produced. Where the real cultivation of soybean includes recycling of 50 % of the trash, this scenario includes 100 % of the trash for upgradation. The recycling of 50 % trash for fertilisation is a real-process parameter that hinders the energy recovery of the crop.

Group 2 are the upgradation scenarios of the soybean crop to biodiesel in a realistic refinery:

- Scenario 2.1 represents a production plant where no biomass is combusted for process steam and electricity—these energy inputs are derived from fossil fuel only.
- Scenario 2.2 considers the combustion of all of the available trash for cogeneration (50 % retrieved from the field where the remaining 50 % is used as a fertiliser).
- Scenario 2.3 considers the maximum production of surplus electricity, where all of the by-products and co-products are sent to cogeneration (including soybean hulls, meal, glycerol, and available trash).

Scenario 3 and Scenario 4 represent the end-use of the soybean biodiesel and plant respectively:

- Scenario 3 considers that the biodiesel produced is used in an internal combustion engine and converted to mechanical energy—this is the predominant intended end-use of liquid biofuels. Scenario 3 is based on Scenario 2.2 because this is representative of the operation of a realistic plant, where the co-products (meal, hulls, and glycerol) are sold in separate markets to maximise economic feasibility and only the waste soybean trash is burnt for process steam and electricity.
- Scenario 4 is where no valorisation of the soybean crop to biodiesel occurs, but where the entire available crop is burnt to generate electricity.

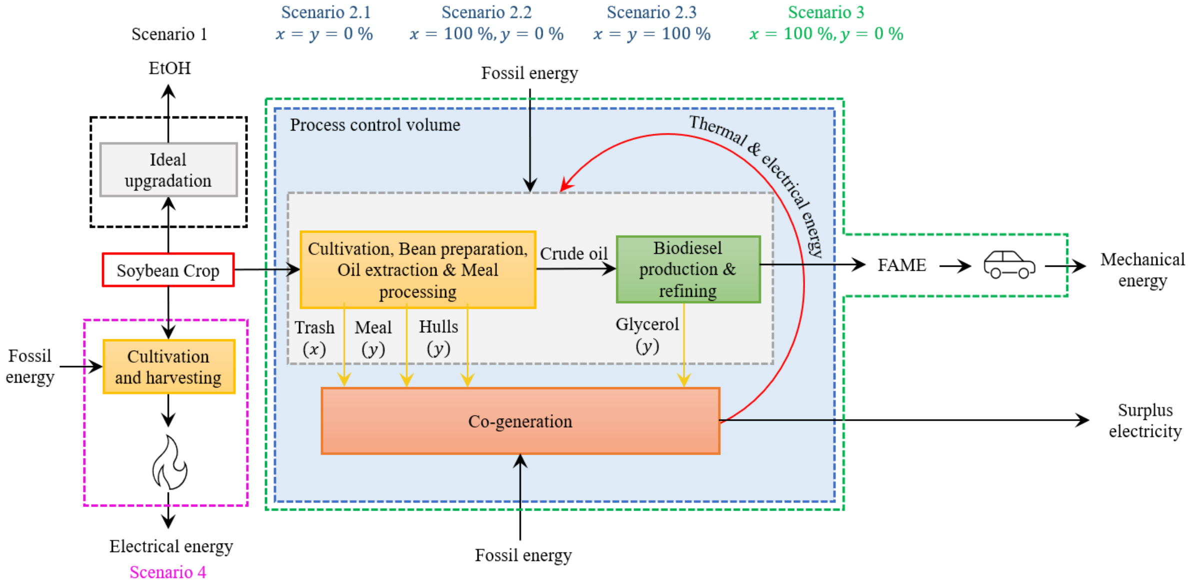


Figure 4.2: Summary of the scenarios evaluated for biodiesel production.

4.6.2 Bioethanol scenarios

As with the soybean model, four groups of Scenarios are evaluated for the sugarcane-bioethanol (SBE) process (see Figure 4.3 for reference):

- Scenario 1 represents the ideal upgradation of sugarcane to bioethanol.

Group 2 are real scenarios that focus on the production of bioethanol and the amount of excess electricity that may be produced.

Group 2A for bioethanol is intended to compare the energy metrics of the standalone 1G and 2G processes, and the integrated 1G-2G model without any energy recovery from the lignocellulose by-products:

- Scenario 2-1G is the 1G bioethanol process without the cogeneration of trash or bagasse.
- Scenario 2-2G is the standalone 2G process without cogeneration of lignocellulose.
- Scenario 2-1G2G is the integrated 1G and 2G process without cogeneration of lignocellulose.

Group 2B evaluates a more optimised bioethanol plant. Cogeneration of lignocellulose is considered and the model parameters are varied to evaluate the optimal configuration of converting the lignocellulose to bioethanol *vs.* process steam and electricity:

- Scenario 2.1 represents the 1G bioethanol production where all of the available trash and bagasse are used to generate process steam and electricity. This is representative of traditional bioethanol facilities that combust the lignocellulosic material in cogeneration.
- Scenario 2.2 is the integrated 1G and 2G facility that is at the point of energy self-sufficiency. Just enough trash and bagasse is burnt to replace the fossil fuels required by the boiler.
- Scenario 2.3 considers the maximum bioethanol production in a realistic scenario. All of the trash and bagasse are valorised to bioethanol in the integrated 1G and 2G process. The only lignocellulose sent to cogeneration is the cellulignin (a by-product of the 2G process). Therefore, fossil fuels are required for the boilers to supplement the process energy requirements.

Groups 3 and 4 take into account the end-use of the biofuel or the initial biomass crop:

- Scenario 3 is based on the parameters of Scenario 2.2— the 1G and 2G energy autonomous process. This scenario is intended to evaluate the use of bioethanol in an internal combustion engine to represent the end-use of the fuel.
- Scenario 4 assesses the conversion of the biomass crop directly to electricial energy, where no biofuel is produced. This scenario is intended to represent a theoretical end-use of the biomass crop.

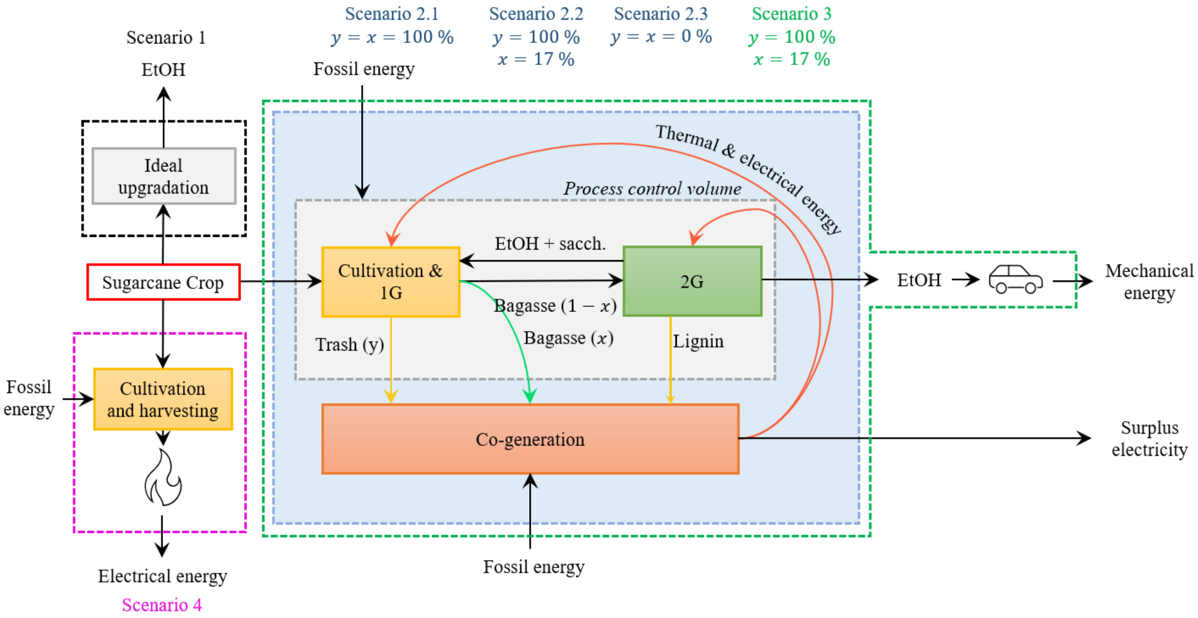


Figure 4.3: Summary of the scenarios evaluated for bioethanol production.

Chapter 5: Results and discussion

5.1 Ideal conversion of biomass to biofuels (Scenario 1)

The theoretical upgradation of the cultivated sugarcane and soybean crop is illustrated in Figure 5.1. The ternary diagram shows the hypothetical maximum mass yield for the biomass-to-biofuel conversion, and the average composition of the waste products. The mass yield (η), and consequently, the change in energy quality (ΔE_{Q}) and the change in energy yield (ΔE_{η}) are calculated from the tie lines. For this exercise, the entire crop is taken as the input for the ideal conversion process. This includes all of the trash. The trash left on the field after harvesting (50 wt. %) is considered as a real process parameter.

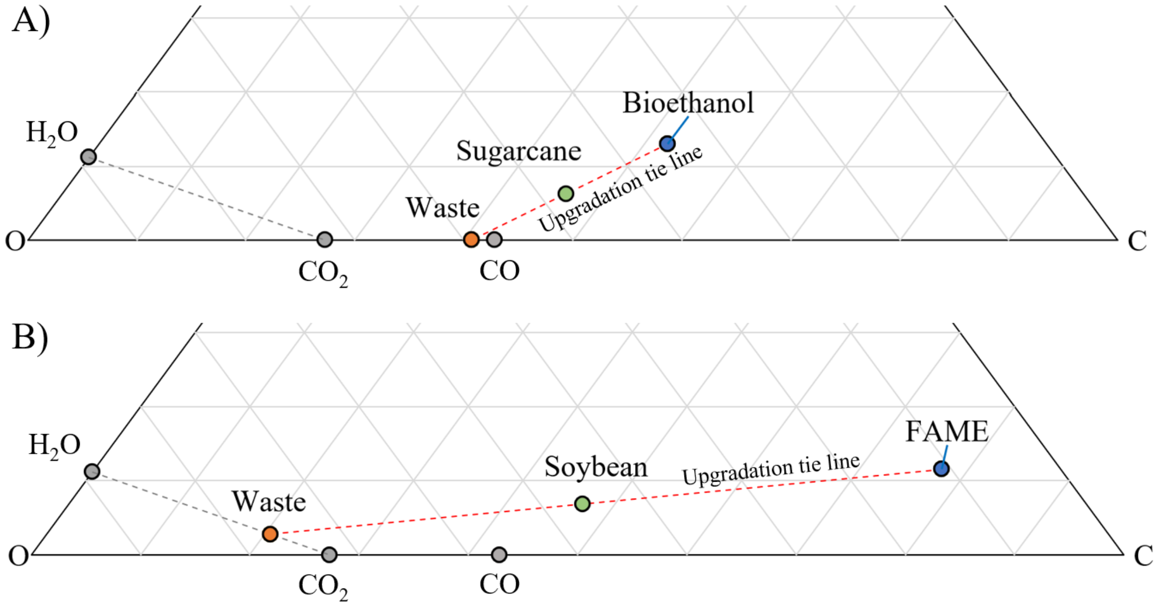


Figure 5.1: Ternary diagram showing the ideal conversion of the sugarcane crop to bioethanol (A) and the soybean crop to FAME (B). *The compositions are plotted on a mass and daf basis.*

The waste products/upgradation losses do not represent a single compound. Rather, the upgradation losses represent the minimum loss of energy-containing carbon and hydrogen in order achieve the maximum mass yield of the biofuel from the biomass:

- The sugarcane crop may undergo decarbonylation and decarboxylation to produce bioethanol, where CO and CO_2 are removed from the feedstock respectively.

- The soybean crop may undergo decarboxylation and dehydration to produce biodisel, where CO_2 and H_2O are removed from the feedstock respectively.

Table 5.1 indicates the mass compositions of the feedstock and products, as well as the theoretical mass yield, change in energy quality, and change in energy yield.

Table 5.1: Results from the ideal valorisation of the soybean and sugarcane plant. *The upgradation losses are a combination of H_2O, CO_2, CO, or C.*

Component	C (wt. %)	H (wt. %)	O (wt. %)	η (%)	ΔE_Q (%)	ΔE_η (%)
Soybean crop	47	7	46	-	-	-
FAME	78	12	11	47	107	97
Upgradation losses	20	3	77	53	-100	0
Sugarcane crop	46	6	47	-	-	-
Bioethanol	52	13	35	48	63	79
Upgradation losses	41	0	59	52	-100	0

The removal of oxygen in the form of water, carbon dioxide, and/or carbon monoxide results in an increase in the oxidation potential of the product from the feed $\left(\frac{m_{O_2|p}}{m_{O_2|f}} > 1\right)$, and therefore, the energy quality increases. The removal of oxygen from the feed in the form of CO_2 is preferred; when the goal is to increase energy density, H/C ratio should be maximised.

Even though the theoretical maximum for η for the biofuels is 47 %–48 %, the ΔE_Q and ΔE_η achieved is relatively high. This is because the higher heating value (HHV) of the biofuel is greater than that of the feed:

- For FAME, the ΔE_Q is 107 %. This is due to the fact that the HHV of biodiesel is more than double that of the feed (-40 MJ kg^{-1} *vs.* -19 MJ kg^{-1}). The ΔE_η is also high (97 %). This is as a result of Equation 2.7 which shows that ΔE_η is a function of the mass yield and the change in energy quality. Theoretically, almost all of the original energy contained in the soybean feedstock can be recovered in biodiesel.
- For bioethanol, the ΔE_Q is 63 %. The change in energy quality for bioethanol is much lower than that of biodiesel due to the lower HHV of bioethanol (-29 MJ kg^{-1}) *vs.* biodiesel (-40 MJ kg^{-1}). The ΔE_η for bioethanol production (79 %) is lower than that of biodiesel production for the same reason.

The ideal conversion results are used as baseline against which the real scenarios are compared.

5.2 Evaluating the configurations of biodiesel production (Scenarios 2.1–2.3)

5.2.1 The cumulative ΔE_{Q} and η for soybean to biodiesel production

The change in energy quality, ΔE_{Q}, *vs.* the mass yield yield, η, for the biodiesel production process (Scenarios 2.1–2.3) is shown in Figure 5.2 and Table 5.2. The change in energy quality has been defined in such a way so as to only consider the recoverable material streams that contribute to the production of the biofuel. ΔE_{Q} communicates whether the feedstock has been upgraded into a more energy dense carrier. The difference among Scenarios 2.1, 2.2, and 2.3 is merely the diversion of the waste/co-products to cogeneration which has no effect on the biodiesel yield. Hence, all 3 scenarios achieve the same plot.

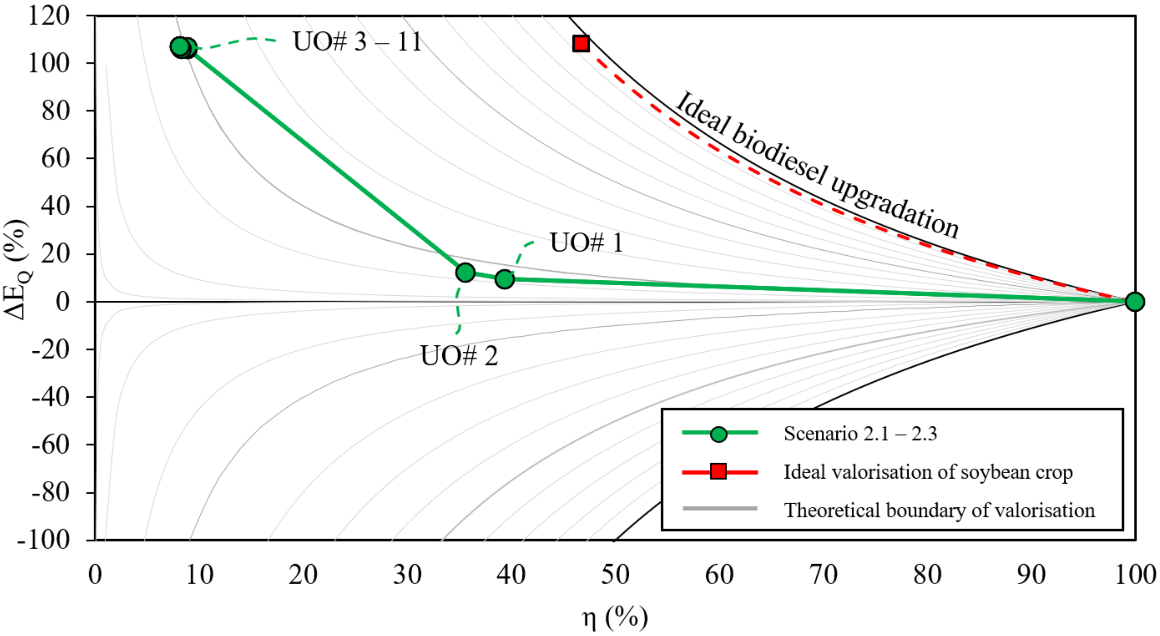


Figure 5.2: The cumulative ΔE_{Q} for biodiesel production. *The output of each process stage is indicated by a marker, where the unit operation number (UO#) is defined in Table 5.2.*

Table 5.2: ΔE_{Q} and η for Group 2 of biodiesel production scenarios.

No.	Unit operation	η	ΔE_{Q}
1	Harvesting	39	9
2	Bean pretreatment	36	12
3	Oil extraction	36	106
4	Oil and solvent recovery	9	106
5	Degumming	9	107
6	Hull and meal processing	9	107
7	Oil pretreatment	8	106
8	Transesterification	8	106
9	Fame purification	8	107
10	Glycerol and methanol recovery	8	107
11	Cogeneration	8	107

The immediate impression presented by Figure 5.2 is the substantial loss of mass. A final η of only 8 % is achieved: a 39 % difference between the real and the ideal case. The mass loss is predominantly attributed to the loss of soybean trash (61 % mass loss after harvesting), hulls (3 % mass loss after bean pretreatment) and the meal (27 % loss of mass after oil extraction). The crude oil is the desirable feedstock for the transesterification process. However, the isolation of the crude oil from the original biomasss yields only 9 % of the original mass. The process only encounters a further 0.6 % reduction in mass yield to obtain the final biofuel (despite the extensive operations required). It is important to note that the addition of methanol during transesterification is accounted for.

Although the soybean co-produts (hulls, meal, and glycerol) are still value added products with necessary markets, for biodiesel production, soybeans are cultivated for the recovery of crude oil. The oil makes up only a small fraction of the soybean crop which puts into question the suitability of the feedstock in the context of land-use change, resource allocation, and process efficiency.

In terms of the increase in energy density, the ΔE_{Q} progressively increases as more lignocellulose is removed: the trash, hulls, and meal have a far lower HHV than the crude oil (see Table 5.3). The increase in ΔE_{Q} is therefore only as a result of refining the biomass rather than from chemical processing. After oil extraction, ΔE_{Q} increases by 106 %. Thereafter, ΔE_{Q} only increases by a further 1 % to achieve an HHV of -40.0 MJ kg^{-1} of biodiesel. Almost no improvement in energy density is achieved after transesterification and purification. The benefit of converting the oil to FAME is the reduction of viscosity which make biodiesel suitable for use in internal combustion engines. Comparatively, the bioethanol process achieves a substantial increase in ΔE_{Q} during the fermentation stage where the desirable feedstock (saccharides) are converted to ethanol—see Section 5.3.2.

Table 5.3: Higher heating value (daf basis) for the unharvested soybean crop, the straw, meal, hulls, crude oil, and biodiesel.

	Soybean crop	Straw	Meal	Hulls	Crude Oil	Biodiesel
$\Delta_c h^\circ\vert_{\mathrm{HHV}}$	-19.2	-18.1	-15.3	-15.6	-39.7	-40.0

5.2.2 The cumulative ΔE_η and η for soybean to biodiesel production

The change in energy yield, ΔE_η, vs the mass yield, η, is determined on a cumulative basis to assess how much energy is transferred from the feedstock to the biofuel and in other useful-forms (electricity). The energy yield also takes into account the energy consumption that the process incurs for the biomass-to-biofuel conversion. The results of Scenario 1, 2.1, 2.2, and 2.3 are shown in Figure 5.4 and Table 5.4:

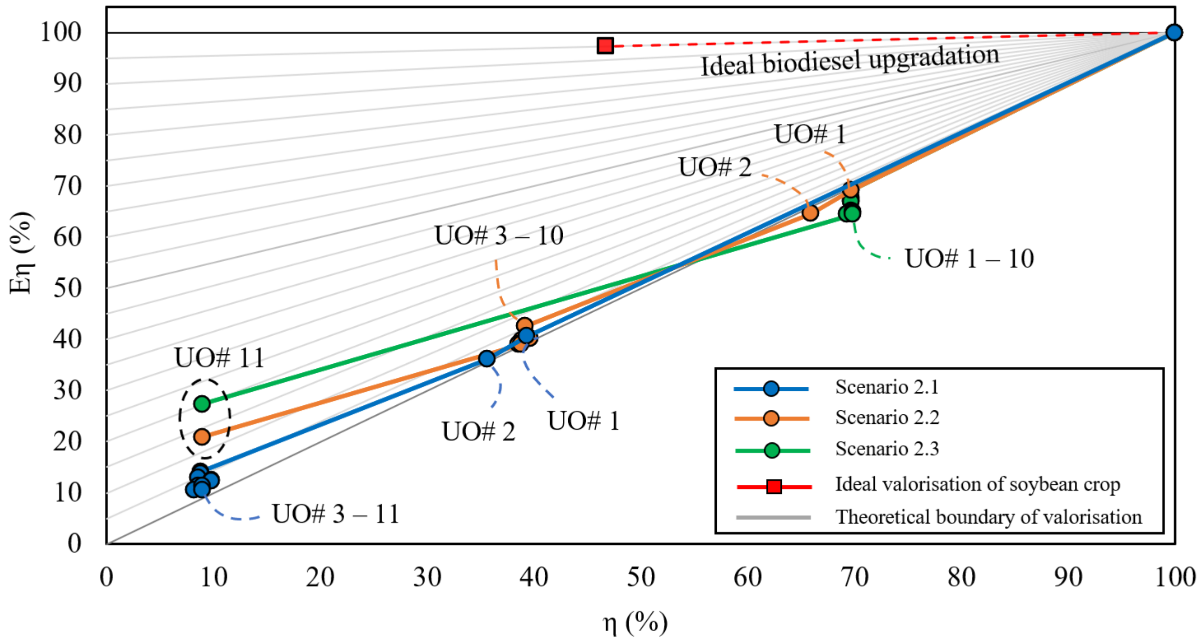


Figure 5.3: The cumulative ΔE_η for biodiesel production. *The output of each process stage is indicated by a marker, where the unit operation number (UO#) is defined in Table 5.4.*

Table 5.4: Comparison of η and ΔE_η for Group 2B of biodiesel scenarios.

No.	Unit Operation	Scenario 2.1		Scenario 2.2		Scenario 2.3	
		η	ΔE_η	η	ΔE_η	η	ΔE_η
1	Harvesting	39	41	70	69	70	69
2	Bean pretreatment	36	36	66	65	70	68
3	Oil extraction	9	14	39	43	70	67
4	Oil and solvent extraction	9	14	39	42	70	67
5	Degumming	9	13	39	42	70	67
6	Hull and meal processing	9	11	39	40	70	65
7	Oil pretreatment	8	11	39	39	69	64
8	Transesterification	10	13	40	40	70	65
9	Fame purification	10	12	40	40	70	65
10	Glycerol and methanol recovery	9	11	39	39	70	65
11	Cogeneration	9	10	9	21	9	27

After the harvesting stage, the ΔE_η is 41 % for Scenario 2.1 and 69 % for Scenario 2.2 and 2.3. When half of the trash is recovered from the field and converted to electricity, ΔE_η has increases by 70 % from Scenario 2.1 to Scenario 2.2/2.3. The recovery of straw, therefore, increases the energy recovery of the process to a large extent.

To substantiate this point, the amount of available trash needed for self-sufficiency (no fossil fuel consumption) was determined: only 17 % of the available trash is required for cogeneration to reach energy autonomy, where no hulls, meal, or glycerol is combusted.

After the oil extraction stage, the ΔE_η achieved is 14 % for Scenario 2.1, 43 % for Scenario 2.2 and 67 % for Scenario 2.3. Of course, the energy yield increases as more waste and co-products are recovered for cogeneration (trash, meal, hulls, and glycerol).

After the recovered biomass is burnt in cogeneration stage, the final ΔE_η is only 10 % for Scenario 2.1, 21 % for Scenario 2.2, and 27 % for Scenario 2.3. Evidently, for Scenario 2.2 and Scenario 2.3, there is a large reduction in ΔE_η after the recovered by- and co-products are combusted for process steam and electricity (from UO# 10–11). The observation is explained by the low energy conversion of biomass to electricity which essentially encompasses the life-cycle of biomass-to-electricity conversion.

It is quite clear that the recovery of the waste- and by-products contribute meaningfully to ΔE_η. The energy consumption of the process, however, has a minor effect. The energy consumed during the process is only 6.9 % of the energy contained in the feedstock.

Comparatively, the energy of the straw, meal, hulls, and glycerol is 83 % of the feedstock. Optimising unit operations would therefore have a marginal improvement in ΔE_η compared to improving the utilisation of waste and by-products. Even though cogeneration exhibits low conversion efficiencies (below 30 %), utilising lignocellulose for cogeneration achieves a 100 % and 161 % increase in ΔE_η for Scenario 2.2 and 2.3 compared to Scenario 2.1.

Even with the complete recovery of the by- and co-products, the final ΔE_η is far below that of the ideal case (97 %). The energy recovered from the soybean biomass in the real-life scenarios is only 10 %–27 % of the ideal ΔE_η. The composition of the soybean crop does not lend itself to efficient biodiesel recovery through transesterification.

To highlight this point, the overall η and ΔE_η were compared for two different system boundaries of Scenario 2.1:

1. The standard system boundary already evaluated (soybean crop to FAME)
2. The boundary from crude oil to FAME—crude oil is taken as the input into this process

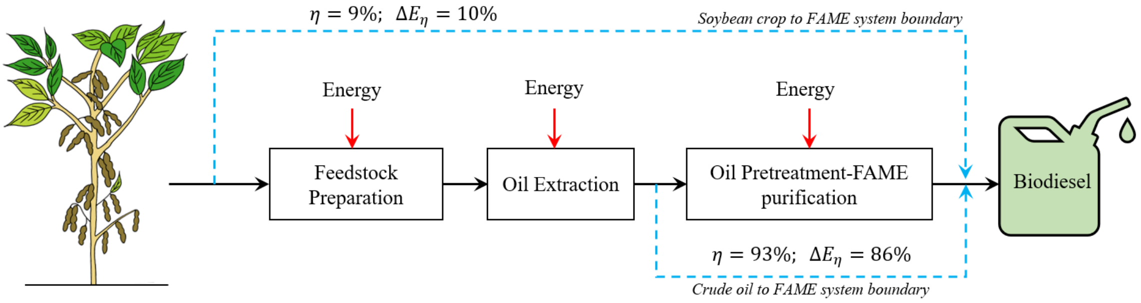


Figure 5.4: The overall η and ΔE_η for biodiesel production from the soybean crop and the crude oil. *The results are based on Scenario 2.1 where there is no recovery of the co- and by-products for cogeneration.*

When crude oil is taken as the input into the process, the results appear more favourable: η of 93 % and ΔE_η of 86 %. The comparison illustrates the energy inefficiency of utilising the soybean crop for FAME production. Using waste cooking oil for biodiesel production would yield far more favourable results than upgrading the soybean crop. Waste cooking oil does, of course, have a different chemical composition to soybean crude oil which would require further pretreatment before transesterification.

The above discussion highlights the unsuitability of the cultivated soybean crop for biodiesel production. The biomass is largely made up of lignocellulose which cannot be converted to biodiesel through industrial transesterification processes. Consequently, there is a large loss in mass that cannot be recovered in the FAME. From a sustainability perspective, the large loss in mass and energy yield essentially indicates the wasted allocation of agriculture for biofuel production which has a pronounced effect on land-use change and the food-energy nexus of the globe.

To improve the energy metrics on an industrial level, the commercialisation of alternative methods of lignocellulose upgradation is required. These methods could involve the use of oleaginous microorganisms for biodiesel production, pyrolysis of biomass by-products for the production of pyrolysis oil, or second generation processing (hydrolysis) of biomass to bioethanol.

5.3 Evaluating the configurations of bioethanol production (Group 2A and 2B)

5.3.1 Comparison of the standalone and integrated 1G and 2G processes (Group 2A)

The overall mass yield, change in energy quality, and the change in energy yield for Scenarios 2-1G, 2-2G, and 2-1G2G are shown in Figure 5.5.

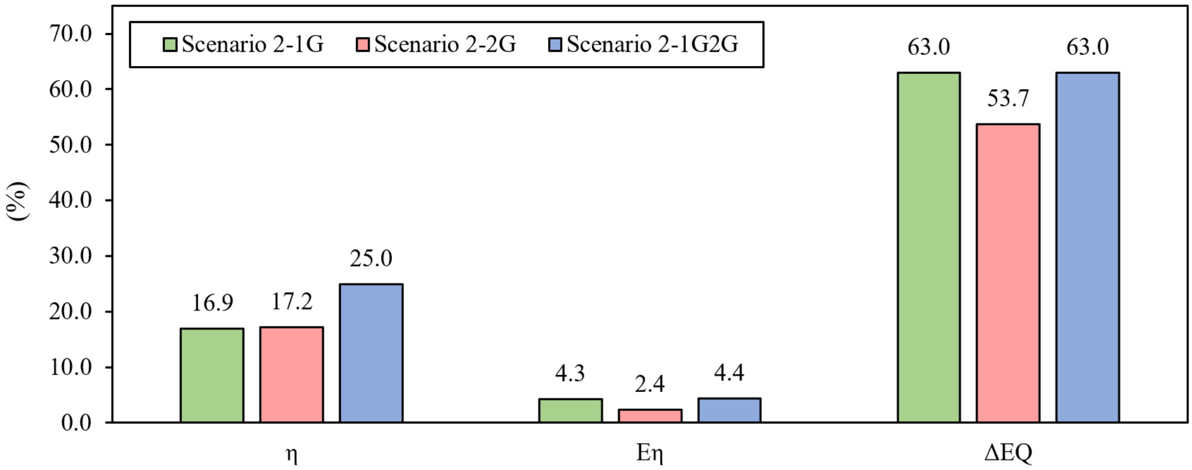


Figure 5.5: Results for Group 2A of sugarcane-bioethanol production. *The standalone 1G and 2G process, and the integrated 1G and 2G process of bioethanol production is mdoelled without the contribution of cogeneration of the by-products.*

It should be noted that for Scenario 2-1G and Scenario 2-1G2G, the input into the process is the sugarcane stalk, as with all other scenarios. However, the input into Scenario 2-2G is the lignocellulose (the sugarcane trash and bagasse only). This was chosen to evaluate the efficacy of a standalone 2G bioethanol process that valorises waste compared to a process that receives raw sugarcane. The system boundaries are illustrated in Figure 5.6:

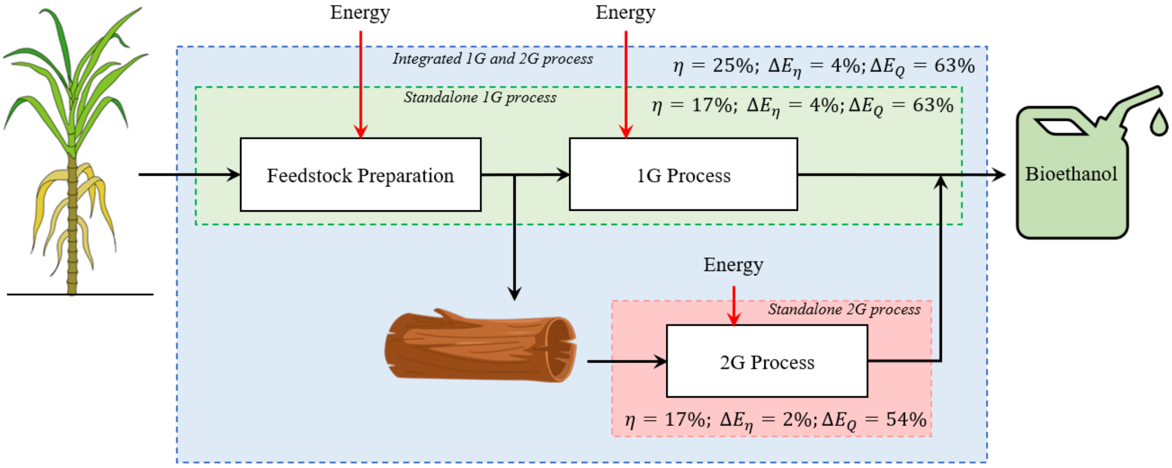


Figure 5.6: Results and illustration of system boundaries for Group 2A of bioethanol

The mass yield achieved for Scenario 2-1G and Scenario 2-2G is almost identical (≈17 %). However, the energy yield for the standalone 1G process is almost twice that of the standalone 2G process (4 % *vs.* 2 %). This result is explained by considering the input into the respective processes as well as the energy consumption.

The sugarcane into the process has a lower HHV than the lignocellulose, which is the feedstock for the 2G process (-17.8 MJ kg^{-1} *vs.* -18.8 MJ kg^{-1}). Consequently, the change in energy quality achieved for 2G production is lower than that for 1G production (54 % *vs.* 63 %). For Scenario 2-1G, the energy consumption is 20 % of the energy contained in the feedstock. For Scenario 2-2G, however, the value is 46 %. The steam explosion operation has a significantly high energy consumption for the 2G process. The higher energy consumption and lower ΔE_Q results the standalone 2G process achieving a lower ΔE_η than the standalone 1G process (2 % *vs.* 4 %) as less energy is recovered per unit of energy of the original feedstock.

For the integrated process (Scenario 2-1G2G), the mass yield increases by 48 % from the standalone 1G process. Of course, the trash and bagasse make up a large portion of the harvested sugarcane (63 wt. %, daf basis). When valorised for bioethanol production, a large improvement in bioethanol recovery is seen.

However, the change in energy yield exhibits a marginal increase for Scenario 2-1G *vs.* Scenario 2-1G2G (4.3 % *vs.* 4.4 %) despite the increased mass yield of bioethanol. This is due to the smaller ΔE_η achieved for the standalone 2G process, as well as high process energy consumption of the 2G process.

Considering the above, the development of 2G bioethanol production and the commercialisation thereof may be beneficial for bioethanol recovery. In terms of energy recovery, the results are less optimal where insignificant improvements are encountered in the overall process.

The above discussion is based on the process configuration where there is no cogeneration of biomass to produce process steam or electricity. Cogeneration is considered for Group 2B in the following subsection.

5.3.2 The cumulative ΔE_Q and η for sugarcane to bioethanol (Group 2B)

The change in energy quality, ΔE_Q, *vs.* mass yield, η, for sugarcane bioethanol production (Scenario 2.1–2.3) is shown in Figure 5.7 and Table 5.5.

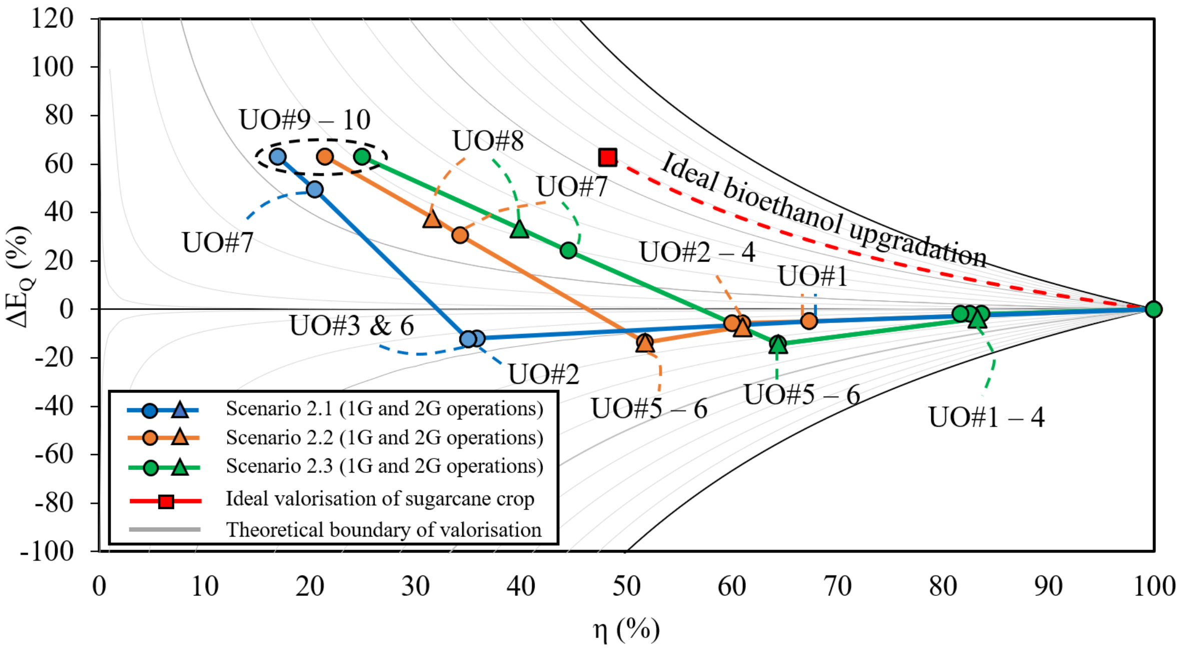


Figure 5.7: The cumulative ΔE_Q for bioethanol production—Group 2B. *The output of each process stage is indicated by a marker, where the unit operation number (UO#) is defined in Table 5.5.*

Table 5.5: Comparison of η and ΔE_{Q} for Group 2B of bioethanol scenarios.

No.	Unit Operation	Scenario 2.1		Scenario 2.2		Scenario 2.3	
		η	ΔE_{η}	η	ΔE_{η}	η	ΔE_{η}
1	Harvesting	67	-5	67	-5	84	-2
2	Milling and Cleaning	36	-12	61	-6	83	-2
3	Pretreatment	35	-13	60	-6	82	-2
4	Steam explosion (2G)	-	-	61	-7	83	-4
5	Enzymatic hydrolysis (2G)	-	-	52	-14	64	-14
6	Evap. and sterilisation	35	-13	52	-14	64	-14
7	Glucose fermentation	20	49	34	30	44	24
8	Xylose fermentation (2G)	-	-	32	38	40	34
9	Distillation and dehydration	17	63	21	63	25	63
10	Cogeneration	17	63	21	63	25	63

For the harvesting stage in Scenarios 2.1 and 2.2, there is a large drop in η (33 %) as the sugarcane trash is not valorised to the biofuel. Comparatively, there is only a drop in 16 % in mass yield for Scenario 2.3 as all of the available sugarcane trash (50 % of the total trash) is recovered for bioethanol production. The ΔE_{Q} also increases between Scenario 2.1 and 2.2 compared to Scenario 2.3 after harvesting. Sugarcane trash has a higher HHV than the stalk (-19.5 MJ kg^{-1} *vs.* -16.9 MJ kg^{-1}). When the trash is not recovered, there is a loss of energy-dense material which results in a decrease in ΔE_{Q} of the recovered material, and of course η.

The $\Delta_c h^{\circ}|_{\mathrm{HHV}}$ for the main desirable streams/components are shown below to validate the discussion:

Table 5.6: Higher heating value (daf basis) for the unharvested surgacane crop, the straw, bagasse, stalk, glucose, and bioethanol.

	Sugarcane crop	Straw	Bagasse	Stalk	Glucose	Bioethanol
$\Delta_c h^{\circ}|_{\mathrm{HHV}}$	-17.8	-19.5	-18.4	-16.9	-14.8	-29.0

A similar result is seen for the milling stage. The sugar-rich juice is extracted after milling leaving bagasse to be recovered for bioethanol or burnt for process energy. Where more bagasse is recovered for fuel production, η and ΔE_{Q} increase.

For the 2G processing stages (steam explosion and enzymatic hydrolysis), there are only small losses in mass and a small reduction in energy quality (Scenario 2.2 and 2.3). These stages therefore exhibit marginal losses in energy dense material.

The most significant increase in ΔE_{Q} is encountered during the fermentation of glucose. There is a 269 %–495 % increase in ΔE_{Q} during this operation. Intuitively, the fermentation step is the only stage in the bioethanol process where there is a chemical upgradation of the feedstock to a product of higher HHV. The HHV of ethanol is far higher than that of glucose (-29.0 MJ kg^{-1} *vs.* -14.8 MJ kg^{-1}). However, during fermentation, there is a drop in mass yield. This is due to the fermentation reaction (Equation 3.2) where CO_2 is released; there is a reduction in the mass of bioethanol from the sugar feed. Any increase in energy density is accompanied with a decrease in mass. The same logic applies for the 2G xylose fermentation step.

We see a final increase in the change in energy quality after the purification of the sterilised wine. Here, the residual sugars and lignocellulose are separated from the ethanol, thereby increasing the final HHV.

5.3.3 The cumulative ΔE_{η} and η for sugarcane to bioethanol (Group 2B)

ΔE_{η} *vs.* η for Scenarios 2.1, 2.2, and 2.3 are shown below. As for biodiesel, the mass yield associated with ΔE_{η} takes into account all biomass that is recovered for biofuel production and/or process heat and electricity.

For all scenarios, the energy metrics are relatively similar for all feed preparation and pretreatment processes (UO#1–6). The similar results in the energy metrics are realised because the by-products in all scenarios are either recovered for bioethanol production or cogeneration. The recovered biomass is reflected in ΔE_{η} and η regardless of the end-use. Differences in the change in energy yield and mass yield will only arise due to the inefficiencies associated with the biofuel conversion process or combustion process.

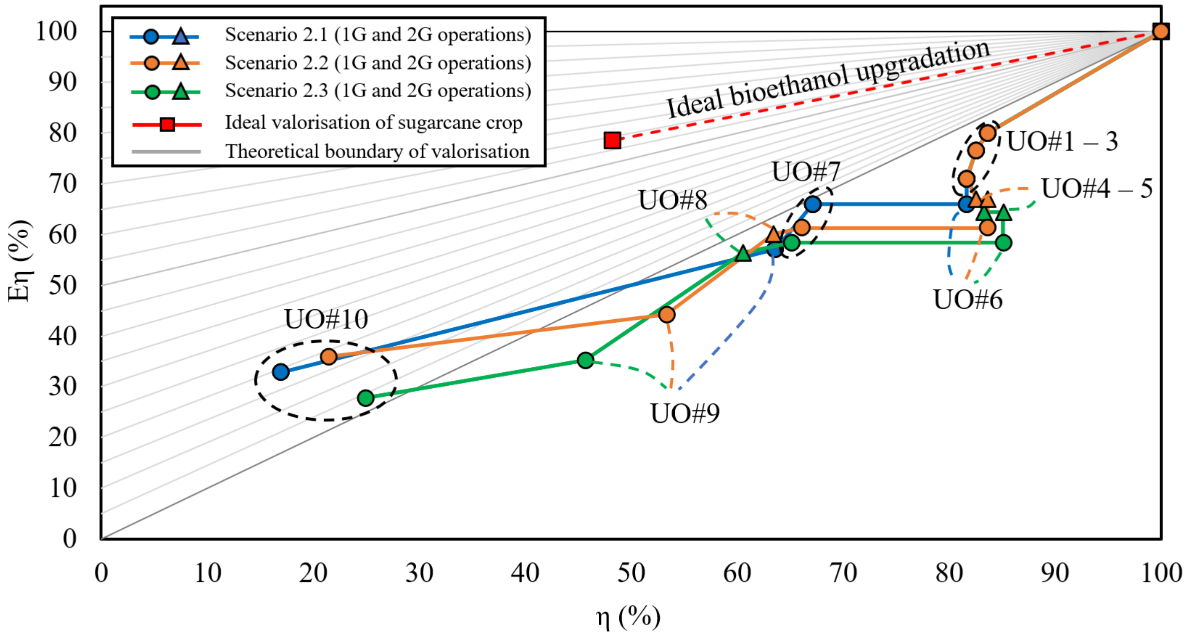


Figure 5.8: The cumulative ΔE_η for bioethanol production—Group 2B. *The output of each process stage is indicated by a marker, where the unit operation number (UO#) is defined in Table 5.7.*

Table 5.7: Comparison of η and ΔE_η for Group 2B of bioethanol scenarios.

No.	Unit Operation	Scenario 2.1		Scenario 2.2		Scenario 2.3	
		η	ΔE_η	η	ΔE_η	η	ΔE_η
1	Harvesting	84	80	84	80	84	80
2	Milling and Cleaning	83	77	83	77	83	77
3	Pretreatment	82	71	82	71	82	71
4	Steam explosion (2G)	-	-	83	67	83	64
5	Enzymatic hydrolysis (2G)	-	-	84	67	85	64
6	Evap. and sterilisation	82	66	84	61	85	58
7	Glucose fermentation	67	66	66	61	65	58
8	Xylose fermentation (2G)	-	-	63	60	61	56
9	Distillation and dehydration	64	57	53	44	46	35
10	Cogeneration	17	33	21	36	25	28

There is a slight decrease in the energy yield from for Scenario 2.2 and 2.3 during the 2G pretreatment and hydrolysis steps. The behaviour is due to the associated losses for these operations as well as the high energy consumption for steam explosion (-2683 MJ per tonne lignocellulose processed). The decrease in ΔE_η after evaporation and sterilisation is due to the energy consumption entirely (-337 MJ per tonne sugarcane processed).

After the distillation and dehydration of the ethanol, the mass yield and energy yield is highest for Scenario 2.1 (64 % and 57 % respectively) because all the available lignocellulose has been recovered for cogeneration. Comparatively, a portion of the biomass by-products in Scenario 2.2 and 2.3 have undergone conversion to bioethanol where the process inefficiencies have already been reflected in η and ΔE_η.

After the combustion of the available biomass, the overall results may be compared. The mass yield is expectedly the lowest for Scenario 2.1 (17 %), followed by Scenario 2.2 (21 %) and Scenario 2.3 (25 %). After conversion of lignocellulose to process energy, the only mass remaining is that of the biofuel. Therefore, the mass yield is highest for Scenario 2.3, where bioethanol production is maximised. The maximum in η does not necessarily indicate where ΔE_η will be the highest. The overall optimum of ΔE_η is obtained for Scenario 2.2 (36 %) where the bioethanol production plant is exactly at the point of energy autonomy and where all the excess lignocellulose is used for bioethanol production. In comparison, the ΔE_η for Scenario 2.3 is 28 % and for Scenario 2.1, it is 33 %. Even by maximising the energy recovery through integrating second generation processing (Scenario 2.2), the ΔE_η achieved is only 3 % higher than traditional first generation bioethanol production (Scenario 2.1). There is a marginal increase in energy yield by integrating the 2G process. A techno-economic study would be required to justify the additional infrastructure associated with the 2G production process.

Evidently, converting all available biomass by-products to process heat and electricity (Scenario 2.1) has a more favourable energy recovery than maximising bioethanol production (Scenario 2.3). This sentiment is expanded on in Section 5.3.4, where the sensitivity analysis is evaluated.

The energy consumption for the overall process is about 20 % (Scenario 2.1), 26 % (Scenario 2.2) and 30 % (Scenario 2.3) of the feedstock energy. However, the energy contained in the straw and bagasse is 67 % of the feedstock energy. The energy potential of the lignocellulose has a more significant effect on ΔE_η than just the energy utility of the process operations. In essence, there is a trade-off between utilising waste biomass for bioethanol production and for process energy.

Compared to the ideal route of upgradation, the overall η achieved for all scenarios is only 8 %–12 % of the ideal; and the overall ΔE_η achieved for all scenarios is only 22 %–29 % of the ideal. The energy utility, combined with the process inefficiencies result in poor energy metrics compared to the ideal case.

5.3.4 The point of energy self-sufficiency

Scenario 2.2 for bioethanol production is based on the point where energy self-sufficiency is reached for the processing facility. At this point, the boiler is no longer supplemented by fossil fuels to produce steam and electricity for the plant.

A sensitivity analysis was performed to iteratively solve for this point. First, all the trash is burnt in the boiler and the amount of bagasse sent to cogeneration was increased. All of the trash was combusted first in this model because the trash alone does not release enough energy to completely replace the fossil fuel requirements of the boiler. Therefore, the boiler must be supplemented by all the available trash and some bagasse. The trash was chosen as the first lignocellulose to be combusted as traditional bioethanol plants incinerate the trash for waste disposal regardless.

It was determined that 17 % of the available bagasse (and all of the available trash) must be combusted to obtain a self-sufficient plant. At this point, 83 % of the bagasse is available for 2G bioethanol production.

It is important to note that at the point of energy self-sufficiency, a maximum in the ΔE_η is achieved (36 %), as shown in Figure 5.9. This behaviour is intuitive when taking into account the conversion efficiency achieved for each section of the Figure.

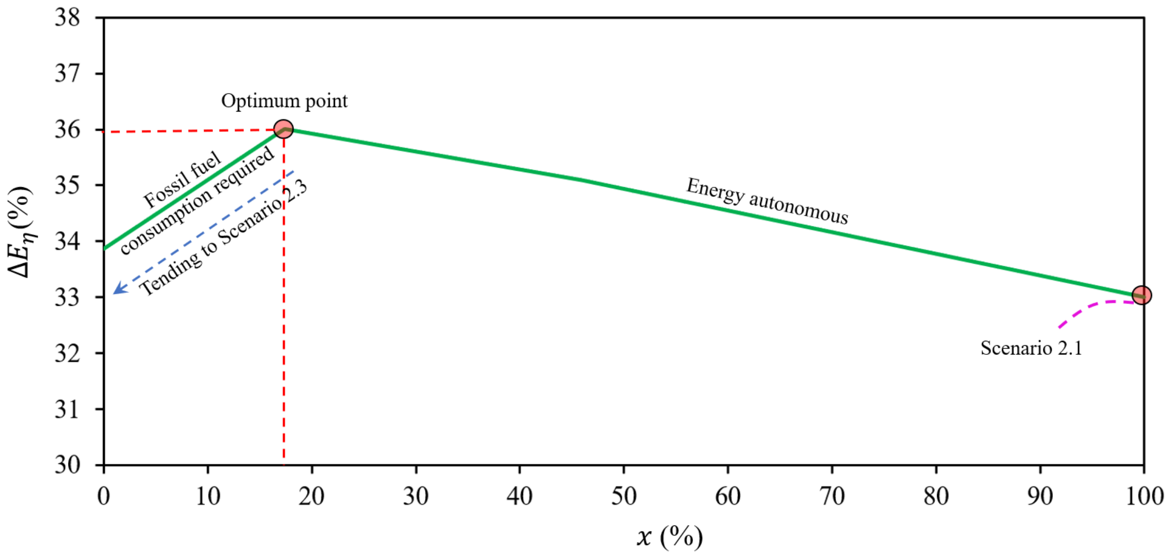


Figure 5.9: The sensitivity analysis performed to determine the amount of bagasse diverted to cogeneration (x) for the optimisation of ΔE_η. *All of the available sugarcane trash is sent to cogeneration for this analysis.*

Before the optimum point, fossil fuels are used to supplement the boiler which reduces the energy yield. As fossil fuels are increasingly replaced with biomass, the energy yield increases. Of course, as more bagasse is diverted away from the 2G process, the steam demand for the 2G process also decreases and the bioethanol production decreases. This indicates that the consumption of fossil fuels and the conversion in the boiler thereof overwhelms the benefit of energy production from the bioethanol yield.

However, after the point of reaching self-sufficiency (optimum point), the energy yield starts to decrease. This behaviour indicates that after the optimum point, the energy produced in the form of electricity is less than the energy yielded from biofuel valorisation, even though the power demand of the 2G process increases along the x-axis.

It is also interesting to note the slopes of the left hand and right hand side of the optimum point. Below the value of $x = 17$ %, ΔE_η tends towards the overall results of Scenario 2.3 at a faster rate (per unit x) than on the right hand side of the optimum point. It is therefore more desirable to have a higher production of excess electricity from process waste biomass than to maximise bioethanol production.

5.4 Cross-process comparison and end-point utilisation

This section aims to evaluate 1) the sugarcane-bioethanol process *vs.* soybean-biodiesel process and 2) the end-use of the biofuels in an internal combustion engine *vs.* the conversion of the feedstock directly to electricity.

5.4.1 Sugarcane to bioethanol *vs.* soybean to biodiesel

To compare the two biofuel production processes, scenarios with similar conditions are considered. Firstly, Scenario 2-1G (for bioethanol) and Scenario 2.1 (for biodiesel) are compared as these are process scenarios with similar conditions. Both scenarios consider 1G production where there is no cogeneration of the biomass co- and by-products. For the overall processes, the bioethanol process achieves almost double the mass yield compared to biodiesel production (17 % *vs.* 9 %). However, the change in energy yield is far less (4 % *vs.* 10 %). The higher ΔE_η for soybean valorisation is attributed mainly to the larger ΔE_Q achieved (107 % for soybean-biodiesel and 63 % for sugarcane-bioethanol) and the lower energy consumption per energy unit of the feedstock (7 % for soybean-biodiesel and 20 % for sugarcane-bioethanol).

The results for ΔE_η change considerably when introducing the complete cogeneration of the biomass co- and by-products (Scenario 2.1 for bioethanol and Scenario 2.3 for biodiesel). ΔE_η increases by 725 % for sugarcane processing and 170 % for soybean processing. Cogeneration of the by-products improve the energy metrics of bioethanol far more than that of biodiesel. To explain the difference, the energy profile of the feedstocks should be considered:

Table 5.8: Energy profile of the soybean and sugarcane crops (unharvested, daf).

Component	Soybean crop MJ MJ^{-1}	Sugarcane crop MJ MJ^{-1}
Straw/trash	57 %	36 %
Processing by- and co-products	24 %	32 %
Biofuel-specific feedstock	19 %	32 %

Straw/trash: the total before harvesting

Processing by- and co-products: the bagasse or meal/hulls recovered after feedstock preparation

Biofuel-specific feedstock: saccharides for bioethanol and oil for biodiesel

The soybean trash constitutes 57 % of the cultivated crop. Whereas for sugarcane, the trash is only 36 %. Both models consider leaving 50 wt. % of the trash on the field for soil fertilisation. The abandonment of half of the straw results in a significant reduction in energy yield. The effect is felt far less for sugarcane to bioethanol production as the straw constitutes less of the crop's total energy.

Through the above discussion as well as the results presented in the previous subsections, it becomes increasingly evident that the composition of the biomass into the process must be considered when evaluating the overall energy efficiency of the process. The energy recovery of biofuel production is far more dependent on the suitability of the feedstock than the utility requirements of the individual unit operations. Sugarcane-bioethanol production is less affected by the feedstock composition because the biomass by-products may undergo the 2G process for bioethanol production. However, soybean lignocellulose by-products cannot undergo industrial transesterification for biodiesel production—the biomass may only be considered for cogeneration. The latter aspect may be improved by considering an integrated biodiesel-bioethanol production plant, or by considering other methods of upgrading the soybean lignocellulose. This, however, is beyond the scope of this study.

5.4.2 The end use of biofuels

Scenario 3 represents the end use of the liquid biofuel in an internal combustion engine which is based on the biofuel production of Scenario 2.2 for both the bioethanol and biodiesel process. Scenario 4, on the other hand, encompasses the direct conversion of the harvested biomass to electricity. The mass yield and change in energy quality is 0 % and -100 %, respectively, for both Scenarios—there is no mass of energy dense material retained after the whole life cycle. Conversely, the energy yield is greater than 0 % as energy is still produced either in the form of mechanical or electrical energy. For Scenario 3, the energy yield is always less than Scenario 2 because conversion inefficiencies are introduced for the end-use of the fuel.

For Scenario 3, the combustion of bioethanol and biodiesel to mechanical energy results in a drop in ΔE_η by 17 % and 19 % respectively. Comparatively, combusting the biomass crop for electricity generation achieves a 3 %–8 % higher energy yield than the crop-to-fuel-to-wheel process. Converting the biomass directly to electricity has a significant increase in energy efficiency in comparison to undergoing biomass valorisation for use in an engine. Of course, this is an abortive comparison as liquid biofuels are a necessary energy storage system for transportation utility. Regardless, this comparison illustrates the magnitude of wasted energy inherent in biomass to biofuel production processes.

Table 5.9: Bioethanol and biodiesel model results.

Scenario	Biofuel produced[1] (kg $\text{ton}^{-1}_{\text{bm}}$)	Electricity surplus[1] (kWh $\text{ton}^{-1}_{\text{bm}}$)	Steam utility[1,3] (kg $\text{ton}^{-1}_{\text{bm}}$)	Excess steam [1,4] (kg $\text{ton}^{-1}_{\text{bm}}$)	η[2] (%)	ΔE_{Q}[2] (%)	ΔE_{η}[2] (%)	Net energy produced[1,5] (MJ $\text{ton}^{-1}_{\text{bm}}$)
Sugarcane bioethanol								
1	185	-	-	-	48	63	79	5357
2-1G	65	36	458	0	17	63	4	291
2.1	65	139	458	346	17	63	33	2244
2.2	82	58	633	0	21	63	36	2456
2.3	96	71	749	0	25	63	28	1896
3	-	58	633	0	0	-100	9	665
4	-	976	0	949	0	-100	12	837
Soybean biodiesel								
1	1099	-	-	-	47	107	97	43971
2.1	164	0	486	0	9	107	10	4116
2.2	164	654	486	2250	9	107	21	8191
2.3	164	1363	486	4649	9	107	27	10743
3	-	654	486	2250	0	-100	8	3268
4	-	6863	-	6680	0	-100	16	5953

ton_{bm}: Ton of biomass processed (*i.e.* soybeans and sugarcane stalk sent to processing plant respectively)

[1] As received basis | [2] Dry and ash free basis

[3] Steam consumed by biofuel production process | [4] Steam expanded in condensing steam turbine for surplus electricity

[5] Net energy: Total energy produced in the form of biofuel/electricity/steam minus the fossil fuel derived energy consumed

5.5 Closing the gap of conventional energy metrics

The fossil energy ratio (FER), the net energy ratio (NER), and the change in energy yield (ΔE_η) are compared for Scenarios 2.1, 2.1, 2.3, 3 and 4 for the soybean biodiesel model (Figure 5.10). The below discussion is applicable to the sugarcane-bioethanol process scenarios as well. Only the soybean-biodiesel results are discussed for simplicity.

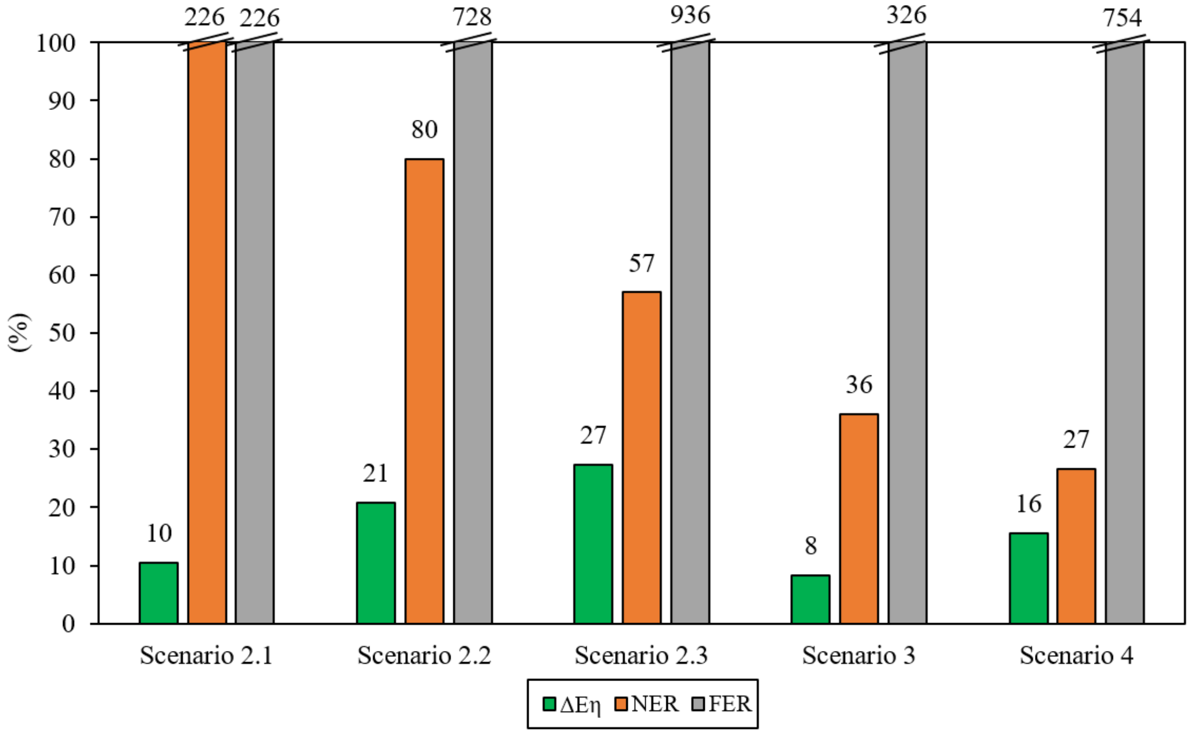


Figure 5.10: The overall values for ΔE_η, NER and FER for the biodiesel model scenarios. *The y-axis is limited to 100 % as some values exceed this limit to such as extent that the comparison would otherwise be diluted.*

The main difference between the definition of life-cycle assessment metrics (FER and NER) and the energy metrics of this study is the reference state of energy consumption. ΔE_η considers the biomass feedstock, in its entirety, as the main energy input. The change in energy yield increases based on the net energy production in reference to the biomass cultivated. In contrast, the NER only considers biomass as an input if it is recovered for conversion to process heat or electricity—the NER does not take into account the biomass utilised for biofuel production. The FER does not consider biomass as an energy cost at all, and only looks at the total energy produced in reference to the fossil fuel consumed.

The FER increases as fossil fuels are increasingly replaced by biomass for the production of process steam and electricity. The FER increases from 226 % (Scenario 2.1), to 728 % (Scenario 2.2) and to 936 % (Scenario 2.3). This parameter communicates that the biodiesel production process produces 2.26–9.36 times more energy than what is consumed in non-renewable fuels. The FER conveys whether the process may overcome non-renewable fuel consumption. This is a fair enough indication of the fossil fuel demand of the process. However, the FER does not convey how efficiently energy is utilised or transferred from the feedstock to the product.

The NER paints a different picture. For Scenario 2.1, the NER is equal to the FER (226 %) as no biomass is consumed for thermal/electrical process energy. As more biomass is diverted to cogeneration, the NER drastically decreases and begins to approach results of the ΔE_η but in an inverse relationship. The NER initially indicates that Scenario 2.1 produces 2.26 times more energy than what is consumed, but reduces to value of 0.57 (Scenario 2.3). The NER is initially high for Scenario 2.1 because the reference of energy consumption is only the fossil fuel. The NER only considers biomass as energy input when biomass is converted to process energy in cogeneration (Scenario 2.2 and Scenario 2.3).

The message of the NER results are counter-intuitive. The NER is meant to give a measure of renewability. However, as our biodiesel production plant becomes more energetically self-sufficient (Scenario 2.1 *vs.* Scenario 2.3), the "renewability factor" dwindles. This illustrates the inherent flaw of excluding the biomass feedstock as a direct energy input at the initial stage of the system boundary.

In contrast, the energy yield, ΔE_η, increases as more biomass waste/co-products are diverted to generate thermal/electrical process energy. When waste/co-product streams that are not valorised are utilised for useful energy (biofuel or electricity), the gain on energy investment is greater.

Lastly, the NER indicates that Scenario 3 is less renewable than Scenario 4 (NER value of 36 % and 27 % respectively). Scenario 3 has far more inefficiencies as it involves valorising the soybean crop to biodiesel and then converting it to mechanical energy. The TTW stage alone has an efficiency of 25 % (where only 25 % of the biodiesel energy is recovered in mechanical energy). Comparatively, the energy conversion of combusting the feedstock directly to electricity is 18 %. There is a small amount of fossil energy consumed in Scenario 4 due to the cultivation and harvesting energy requirements. Again, the NER values provide a false indication of which scenario provides a higher recovery of energy. In contrast, the change in energy yield conveys results which are inline with the process efficiencies (ΔE_η of 8 % and 16 % for Scenario 3 and Scenario 4 respectively).

Of course, the results for NER and FER are not directly comparable with results obtained in life-cycle assessments: the system boundary of this study is different to that of life-cycle assessments; the developed models do not consider the life-cycle energy equivalent of material and energy inputs; and mass or energy allocation methods are not applied.

Regardless, this comparison does serve to identify a gap in the reliability and sensibility of the FER and NER that ΔE_η addresses.

5.6 Food-crop for thought

It would be naive to suggest that all processing operations, biomass- or petroleum-derived, have been developed and adopted because of favourable energy metrics. Dale (2007) presents a compelling argument dispelling the use of energy metrics to evaluate biofuel processes—specifically for the net energy ratio. The author highlights that energy products are refined based on the service they provide, rather than the process efficiency. This is the very reason why global markets value electricity and liquid fuels far more than coal or crude oil; it is the quality of the energy carrier rather than the calorific value that determines the demand.

Even so, analysing ΔE_η provides invaluable insight into the suitability of the feedstock and efficiency of the process. The energy recovered from the feedstock must be understood in the context of the biofuel industry. With the every growing demand for bioethanol and biodiesel, it is energetically inefficient to divert food supplies and agricultural land to biofuels, where small ΔE_η are achieved. This is especially concerning when biomass-derived fuels are considered as a viable substitute for non-renewable fuels. Fossil fuels are demonised for their environmental impact. However, the feedstocks from which they are derived are appropriate for their synthesis (*e.g.*, crude oil and natural gas). Thus, even in the environmental and sociological context, ΔE_η is an imperative starting point to assess the efficacy of fuel synthesis.

Chapter 6: Conclusions and recommendations

This dissertation presents a criticism of industrially employed biofuel production processes and traditional energy metrics. The change in energy quality and the change in energy yield were assessed for the soybean-biodiesel and the sugarcane-bioethanol production processes for various scenarios. The scenarios explored encompass the use of the waste- and by-products for process energy and biofuel production, as well as the end-use of the biofuel and the direct conversion of the biomass crop to electricity.

The ΔE_Q achievable for soybean-biodiesel production is 107 %. Almost the entire increase in ΔE_Q is attributed to extracting the crude oil. The transesterification step does not serve to improve the quality of the fuel, but to produce a fuel with suitable physical characteristics for engines. Even with the large increase in energy density, there is a relatively small recovery of energy in the product relative to the feedstock. ΔE_η for the the biodiesel process is 10 %–27 %, where the change in energy yield increases significantly as more of the waste- and by-products are used in cogeneration. Even with the utilisation of all available by-product streams, ΔE_η is only 28 % of the ideal case. The poor recovery of energy materialises because the soybean crop is only composed of 19 % oil (MJ MJ^{-1}), where the balance is made up of the straw, meal, and hulls.

For the sugarcane-bioethanol process, the ΔE_Q is 63 %. It was shown that for an integrated 1G and 2G bioethanol process, ΔE_η favours the production of process energy from lignocellulose rather than the 2G production of bioethanol. There is an optimum value of ΔE_η (36 %) which is achieved where just enough lignocellulose is used for process energy and the balance for bioethanol production. Even so, the ΔE_η in this case is only 3 % higher than the traditional 1G process where all the lignocellulose is combusted for process energy. Despite the good intentions of maximising bioethanol yield from waste lignocellulose in 2G production, the energy losses indicate that 2G production is simply not worth the energy, especially considering the additional infrastructure required. In terms of the ideal case, Group 2B of the scenarios achieved 35 %–46 % of the ideal ΔE_η, where the ΔE_η for for bioethanol production is far more favourable than the biodiesel process. This is predominantly attributed to the fact that the sugarcane feedstock is composed of less straw.

It was shown that the life-cycle of the feedstock-to-fuel-to-mechanical energy in an internal combustion engine results in more energy losses than converting the biomass feedstock directly to electrical energy. This theoretical exercise depicts the process inefficiencies encountered in production processes.

Regardless of the modelled scenario, food-based crops are not viable feedstocks for fuel upgradation. Even for bioethanol production, upgrading lignocellulose to bioethanol does not provide favourable energy metrics. In comparison, the conversion of crude oil to biodiesel holds a significant improvement. Therefore, the importance of considering the feedstock used for biofuel production cannot be understated.

Finally, the net energy ratio (NER) and the fossil energy ratio (FER) were compared to the ΔE_η for soybean-biodiesel production of Group 2, 3, and 4 of the model scenarios. The NER and FER are shown to be poor metrics for evaluating the energy efficiency of biofuel processes. Although the FER provides an intuitive measure of the renewability of the process regarding fossil fuel consumption, the results become meaningless when biomass is used for process energy. The NER produces results which are counter-intuitive to the essence of a "sustainable" processes—as more biomass is used for cogeneration, the NER decreases. This flaw is inherent to the definition of the NER. It highlights the importance of considering the entire biomass plant as the reference state for an energy-metric-based evaluation.

This study may be extended into various fields of research concerning biomass valorisation. The following is recommended:

1. The integrated bioethanol and biodiesel process may be evaluated based on the change in energy yield and change in energy quality. The sugarcane straw as well as the soybean straw and co-products (meal and hulls) may be used to produce 2G bioethanol. An optimal configuration of these integrated plants may be subsequently determined.
2. The energy metrics may be applied to biofuel production processes for different feedstocks—the suitability of the feedstock, specifically, should be evaluated.
3. This study should be extended into several more biomass valorisation processes (that are not yet commercialised). These include pyrolysis, hydrothermal liquefaction, gasification, and others.
4. The change in energy quality and the change in energy yield should be evaluated in terms of life-cycle assessment system boundaries and parameters. In this regard, the energy metrics may serve to enrich life-cycle assessment studies that intend to quantify energy utilisation and the sustainability of biofuel production.
5. This study has exhibited the inefficiencies encountered in biomass-derived fuel production. Care should be taken when framing biofuels as a promising substitute for non-renewable fuels. Subsequently, the naturally guided biomass-to-fuel synthesis pathways should be assessed against traditional fossil fuel production.

References

Ahmed, I, Decker, J and Morris, D (1994) *How much energy does it take to make a gallon of soydiesel?*, Institute for Local Self-Reliance.

Albuquerque Wanderley, MC de, Martín, C, Moraes Rocha, GJ de and Gouveia, ER (2013) "Increase in ethanol production from sugarcane bagasse based on combined pretreatments and fed-batch enzymatic hydrolysis" *Bioresource technology*, *128*, 448–453.

Almeida, MA de and Colombo, R (2021) "Production Chain of First-Generation Sugarcane Bioethanol: Characterization and Value-Added Application of Wastes" *BioEnergy Research*, 1–16.

Atadashi, I, Aroua, MK, Aziz, AA and Sulaiman, N (2012) "The effects of water on biodiesel production and refining technologies: A review" *Renewable and sustainable energy reviews*, *16*, (5): 3456–3470.

Ayodele, BV, Alsaffar, MA and Mustapa, SI (2020) "An overview of integration opportunities for sustainable bioethanol production from first-and second-generation sugar-based feedstocks" *Journal of Cleaner Production*, *245*, 118857.

Banaszkiewicz, T *et al* (2011) "Nutritional value of soybean meal" *Soybean and nutrition*, *12*, 1–20.

Bell, IH, Wronski, J, Quoilin, S and Lemort, V (2014) "Pure and Pseudo-pure Fluid Thermophysical Property Evaluation and the Open-Source Thermophysical Property Library CoolProp" *Industrial & Engineering Chemistry Research*, *53*, (6): 2498–2508 DOI: `10.1021/ie4033999` eprint: `http://pubs.acs.org/doi/pdf/10.1021/ie4033999` URL: `http://pubs.acs.org/doi/abs/10.1021/ie4033999`.

Bezerra, TL and Ragauskas, AJ (2016) "A review of sugarcane bagasse for second-generation bioethanol and biopower production" *Biofuels, Bioproducts and Biorefining*, *10*, (5): 634–647.

Bizzo, WA, Lenço, PC, Carvalho, DJ and Veiga, JPS (2014) "The generation of residual biomass during the production of bio-ethanol from sugarcane, its characterization and its use in energy production" *Renewable and Sustainable Energy Reviews*, *29*, 589–603.

Borges, ME and Díaz, L (2012) "Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review" *Renewable and Sustainable Energy Reviews*, *16*, (5): 2839–2849.

Borrion, AL, McManus, MC and Hammond, GP (2012) "Environmental life cycle assessment of lignocellulosic conversion to ethanol: a review" *Renewable and Sustainable Energy Reviews*, *16*, (7): 4638–4650.

Borugadda, VB and Goud, VV (2012) "Biodiesel production from renewable feedstocks: Status and opportunities" *Renewable and Sustainable Energy Reviews*, *16*, (7): 4763–4784.

Bose, ML and Martins Filho, JG (1984) "O papel dos resíduos agroindustriais na alimentação de ruminantes" *Informe Agropecuário, Belo Horizonte*, *10*, (119): 3–7.

Branca, C, Di Blasi, C and Galgano, A (2017) "Pyrolytic conversion of wastes from cereal, protein and oil-protein crops" *Journal of Analytical and Applied Pyrolysis*, *127*, 426–435.

Braunbeck, O, Bauen, A, Rosillo-Calle, F and Cortez, L (1999) "Prospects for green cane harvesting and cane residue use in Brazil" *Biomass and Bioenergy*, *17*, (6): 495–506.

Brito, F, Martins, J, Pedrosa, DDR, Monteiro, VDF and Afonso, JL (2013) "Real-life comparison between diesel and electric car energy consumption".

Cabrera, E, Muñoz, MJ, Martín, R, Caro, I, Curbelo, C and Díaz, AB (2015) "Comparison of industrially viable pretreatments to enhance soybean straw biodegradability" *Bioresource Technology*, *194*, 1–6.

Calderan-Rodrigues, MJ, Barros Dantas, LL de, Cheavegatti Gianotto, A and Caldana, C (2021) "Applying molecular phenotyping tools to explore sugarcane carbon potential" *Frontiers in Plant Science*, *12*, 202.

Camargo, JM, Gallego-Rios, JM, Neto, AMP, Antonio, GC, Modesto, M and Leite, JT (2020) "Characterization of sugarcane straw and bagasse from dry cleaning system of sugarcane for cogeneration system" *Renewable Energy*, *158*, 500–508.

Canettieri, EV, Moraes Rocha, GJ de, Carvalho Jr, JA de and Silva, JBdA e (2007) "Optimization of acid hydrolysis from the hemicellulosic fraction of Eucalyptus grandis residue using response surface methodology" *Bioresource Technology*, *98*, (2): 422–428.

Carpio, LGT and Souza, FS de (2017) "Optimal allocation of sugarcane bagasse for producing bioelectricity and second generation ethanol in Brazil: Scenarios of cost reductions" *Renewable energy*, *111*, 771–780.

Carrasco, C, Baudel, HM, Sendelius, J, Modig, T, Roslander, C, Galbe, M, Hahn-Hägerdal, B, Zacchi, G and Lidén, G (2010) "SO2-catalyzed steam pretreatment and fermentation of enzymatically hydrolyzed sugarcane bagasse" *Enzyme and Microbial Technology*, *46*, (2): 64–73.

Carvalho, DJ, Moretti, RR, Colodette, JL and Bizzo, WA (2020) "Assessment of the self-sustained energy generation of an integrated first and second generation ethanol production from sugarcane through the characterization of the hydrolysis process residues" *Energy Conversion and Management*, *203*, 112267.

Castanheira, ÉG, Grisoli, R, Coelho, S, Silva, GA da and Freire, F (2015) "Life-cycle assessment of soybean-based biodiesel in Europe: comparing grain, oil and biodiesel import from Brazil" *Journal of Cleaner Production*, *102*, 188–201.

Castineiras Filho, SLP and Pradelle, F (2020) "Modelling of a Brazilian ethanol plant: impact of the bagasse use and the ethanol dehydration on energy efficiency and sustainability" *Journal of the Brazilian Society of Mechanical Sciences and Engineering*, *42*, 1–25.

Cavalett, O, Junqueira, TL, Dias, MO, Jesus, CD, Mantelatto, PE, Cunha, MP, Franco, HC, Cardoso, TF, Maciel Filho, R, Rossell, CE, *et al* (2012) "Environmental and economic assessment of sugarcane first generation biorefineries in Brazil" *Clean Technologies and Environmental Policy*, *14*, 399–410.

Çengel, YA and Ghajar, AJ (2020) *Heat and Mass Transfer: Fundamentals [and] Applications*, McGraw-Hill Education.

Chang, AF and Liu, Y (2010) "Integrated process modeling and product design of biodiesel manufacturing" *Industrial & Engineering Chemistry Research*, *49*, (3): 1197–1213.

Chongkhong, S, Kanjaikaew, U, Tongurai, C and Yai, H (2012) “A review of FFA esterification for biodiesel production” in: *The 10th International PSU Engineering Conference* vol. 1: pp. 1–5.

Čmolík, J, Schwarz, W, Svoboda, Z, Pokornỳ, J, Réblová, Z, Doležal, M and Valentová, H (2000) “Effects of plant-scale alkali refining and physical refining on the quality of rapeseed oil” *European journal of lipid science and technology*, *102*, (1): 15–22.

Czyrnek-Delêtre, MM, Smyth, BM and Murphy, JD (2017) “Beyond carbon and energy: The challenge in setting guidelines for life cycle assessment of biofuel systems” *Renewable energy*, *105*, 436–448.

Dale, BE (2007) “Thinking clearly about biofuels: ending the irrelevant ‘net energy’debate and developing better performance metrics for alternative fuels” *Biofuels, Bioproducts and Biorefining: Innovation for a sustainable economy*, *1*, (1): 14–17.

De Pretto, C, Tardioli, PW and Costa, CBB (2017) “Assessing energetic and available fuel demands from a soybean biorefinery producing refined oil, biodiesel, defatted meal and power” *Computers & Chemical Engineering*, *104*, 259–270.

Desta, M, Lee, T and Wu, H (2022) “Life cycle energy consumption and environmental assessment for utilizing biofuels in the development of a sustainable transportation system in Ethiopia” *Energy Conversion and Management: X*, *13*, 100144.

Dewulf, J, Van Langenhove, H and Van De Velde, B (2005) “Exergy-based efficiency and renewability assessment of biofuel production” *Environmental science & technology*, *39*, (10): 3878–3882.

Dias, MO, Cunha, MP, Jesus, CD, Rocha, GJ, Pradella, JGC, Rossell, CE, Maciel Filho, R and Bonomi, A (2011) “Second generation ethanol in Brazil: can it compete with electricity production?” *Bioresource technology*, *102*, (19): 8964–8971.

Dias, MO, Cunha, MP, Jesus, CD, Scandiffio, MI, Rossell, CE, Maciel Filho, R and Bonomi, A (2010) “Simulation of ethanol production from sugarcane in Brazil: economic study of an autonomous distillery”, in: *Computer Aided Chemical Engineering*, *28*, Elsevier: pp. 733–738.

Dias, MO, Cunha, MP da, Maciel Filho, R, Bonomi, A, Jesus, CD and Rossell, CE (2011) “Simulation of integrated first and second generation bioethanol production from sugarcane: comparison between different biomass pretreatment methods" *Journal of Industrial Microbiology and Biotechnology*, *38*, (8): 955–966.

Dias, MO, Ensinas, AV, Nebra, SA, Maciel Filho, R, Rossell, CE and Maciel, MRW (2009) "Production of bioethanol and other bio-based materials from sugarcane bagasse: integration to conventional bioethanol production process" *Chemical engineering research and design*, *87*, (9): 1206–1216.

Dias, MO, Junqueira, TL, Cavalett, O, Cunha, MP, Jesus, CD, Mantelatto, PE, Rossell, CE, Maciel Filho, R and Bonomi, A (2013) "Cogeneration in integrated first and second generation ethanol from sugarcane" *Chemical engineering research and design*, *91*, (8): 1411–1417.

Dias, MO, Junqueira, TL, Cavalett, O, Cunha, MP, Jesus, CD, Rossell, CE, Maciel Filho, R and Bonomi, A (2012) "Integrated versus stand-alone second generation ethanol production from sugarcane bagasse and trash" *Bioresource technology*, *103*, (1): 152–161.

Dias, MO, Junqueira, TL, Cavalett, O, Pavanello, LG, Cunha, MP, Jesus, CD, Maciel Filho, R and Bonomi, A (2013) "Biorefineries for the production of first and second generation ethanol and electricity from sugarcane" *Applied Energy*, *109*, 72–78.

Dias, MO, Junqueira, TL, Rossell, CEV, Maciel Filho, R and Bonomi, A (2013) "Evaluation of process configurations for second generation integrated with first generation bioethanol production from sugarcane" *Fuel Processing Technology*, *109*, 84–89.

Dias, MO, Modesto, M, Ensinas, AV, Nebra, SA, Maciel Filho, R and Rossell, CE (2011) "Improving bioethanol production from sugarcane: evaluation of distillation, thermal integration and cogeneration systems" *Energy*, *36*, (6): 3691–3703.

Dunford, N (2016) *Oil and Oilseed Processing III* URL: `https://extension.okstate.edu/fact-sheets/oil-and-oilseed-processing-iii.html#:~:text=Degumming%2C%20deacidification%2Frefining%2C%20bleaching,at%20least%20degummed%20and%20deacidified.` (visited on 10/01/2023).

Duque, A, Álvarez, C, Doménech, P, Manzanares, P and Moreno, AD (2021) "Advanced bioethanol production: from novel raw materials to integrated biorefineries" *Processes*, *9*, (2): 206.

Emiola-Sadiq, T, Zhang, L and Dalai, AK (2021) "Thermal and kinetic studies on biomass degradation via thermogravimetric analysis: a combination of model-fitting and model-free approach" *ACS omega*, *6*, (34): 22233–22247.

Ensinas, AV, Nebra, SA, Lozano, MA and Serra, LM (2007) "Analysis of process steam demand reduction and electricity generation in sugar and ethanol production from sugarcane" *Energy Conversion and Management*, *48*, (11): 2978–2987.

Erickson, DR (2015) *Practical handbook of soybean processing and utilization*, Elsevier.

Fehr, W and Caviness, C (1977) *Stages of soybean development* Iowa Sate University.

Fernando, S, Karra, P, Hernandez, R and Jha, SK (2007) "Effect of incompletely converted soybean oil on biodiesel quality" *Energy*, *32*, (5): 844–851.

Freedman, B, Pryde, E and Mounts, T (1984) "Variables affecting the yields of fatty esters from transesterified vegetable oils" *Journal of the American Oil Chemists Society*, *61*, 1638–1643.

Freedman, B, Butterfield, RO and Pryde, EH (1986) "Transesterification kinetics of soybean oil 1" *Journal of the American oil chemists' society*, *63*, 1375–1380.

Fukuda, H, Kondo, A and Noda, H (2001) "Biodiesel fuel production by transesterification of oils" *Journal of bioscience and bioengineering*, *92*, (5): 405–416.

Fulton, LM, Lynd, LR, Körner, A, Greene, N and Tonachel, LR (2015) "The need for biofuels as part of a low carbon energy future" *Biofuels, Bioproducts and Biorefining*, *9*, (5): 476–483.

Furlan, FF, Tonon Filho, R, Pinto, FH, Costa, CB, Cruz, AJ, Giordano, RL and Giordano, RC (2013) "Bioelectricity versus bioethanol from sugarcane bagasse: is it worth being flexible?" *Biotechnology for Biofuels*, *6*, (1): 1–12.

Furlan, FF, Costa, CBB, Castro Fonseca, G de, Pelegrini Soares, R de, Secchi, AR, Cruz, AJG da and Campos Giordano, R de (2012) "Assessing the production of first and second generation bioethanol from sugarcane through the integration of global optimization and process detailed modeling" *Computers & Chemical Engineering*, *43*, 1–9.

Gharby, S *et al* (2022) “Refining vegetable oils: Chemical and physical refining” *The Scientific World Journal*, *2022*,

Gonzalez, PGA, Jesus Gariboti, JC de, Leal Silva, JF, Lopes, ES, Abaide, ER, Lopes, MS, Concha, VOC, Felisbino, RF, Gomes, EL and Tovar, LP (2023) “Soybean straw as a feedstock for value-added chemicals and materials: recent trends and emerging prospects” *BioEnergy Research*, *16*, (2): 717–740.

Granjo, JF, Duarte, BP and Oliveira, NM (2017) “Integrated production of biodiesel in a soybean biorefinery: Modeling, simulation and economical assessment” *Energy*, *129*, 273–291.

Haas, MJ, McAloon, AJ, Yee, WC and Foglia, TA (2006) “A process model to estimate biodiesel production costs” *Bioresource technology*, *97*, (4): 671–678.

Hau, JL and Bakshi, BR (2004) “Promise and problems of emergy analysis” *Ecological modelling*, *178*, (1-2): 215–225.

Hernández-Salas, J, Villa-Ramírez, M, Veloz-Rendón, J, Rivera-Hernández, K, González-César, R, Plascencia-Espinosa, M and Trejo-Estrada, S (2009) “Comparative hydrolysis and fermentation of sugarcane and agave bagasse” *Bioresource technology*, *100*, (3): 1238–1245.

Hill, J, Nelson, E, Tilman, D, Polasky, S and Tiffany, D (2006) “Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels” *Proceedings of the National Academy of sciences*, *103*, (30): 11206–11210.

Hiloidhari, M, Araújo, K, Kumari, S, Baruah, D, Ramachandra, T, Kataki, R and Thakur, I (2018) “Bioelectricity from sugarcane bagasse co-generation in India–An assessment of resource potential, policies and market mobilization opportunities for the case of Uttar Pradesh” *Journal of cleaner production*, *182*, 1012–1023.

Huang, X, Cao, JP, Zhao, XY, Wang, JX, Fan, X, Zhao, YP and Wei, XY (2016) “Pyrolysis kinetics of soybean straw using thermogravimetric analysis” *Fuel*, *169*, 93–98.

Huo, H, Wang, M, Bloyd, C and Putsche, V (2009) “Life-cycle assessment of energy use and greenhouse gas emissions of soybean-derived biodiesel and renewable fuels” *Environmental science & technology*, *43*, (3): 750–756.

International Energy Agency (2023) *Transport biofuels* URL: `https://www.iea.org/reports/renewables-2023/transport-biofuels` (visited on 05/05/2024).

Jagtap, A and Kalbande, S (2022) "Investigation on pyrolysis kinetics and thermodynamic parameters of soybean straw: a comparative study using model-free methods" *Biomass Conversion and Biorefinery*, 1–12.

Jerzak, W, Reinmöller, M and Magdziarz, A (2022) "Estimation of the heat required for intermediate pyrolysis of biomass" *Clean Technologies and Environmental Policy*, *24*, (10): 3061–3075.

Kamusoko, R, Jingura, RM, Parawira, W and Chikwambi, Z (2021) "Strategies for valorization of crop residues into biofuels and other value-added products" *Biofuels, Bioproducts and Biorefining*, *15*, (6): 1950–1964.

Kanoglu, M and Dincer, I (2009) "Performance assessment of cogeneration plants" *energy conversion and management*, *50*, (1): 76–81.

Karp, SG, Medina, JD, Letti, LA, Woiciechowski, AL, Carvalho, JC de, Schmitt, CC, Oliveira Penha, R de, Kumlehn, GS and Soccol, CR (2021) "Bioeconomy and biofuels: the case of sugarcane ethanol in Brazil" *Biofuels, Bioproducts and Biorefining*, *15*, (3): 899–912.

Khatiwada, D and Silveira, S (2009) "Net energy balance of molasses based ethanol: the case of Nepal" *Renewable and Sustainable Energy Reviews*, *13*, (9): 2515–2524.

Kim, S and Dale, BE (2004) "Global potential bioethanol production from wasted crops and crop residues" *Biomass and bioenergy*, *26*, (4): 361–375.

Kumar, A, Kumar, V, Singh, B, *et al* (2021) "Cellulosic and hemicellulosic fractions of sugarcane bagasse: Potential, challenges and future perspective" *International Journal of Biological Macromolecules*, *169*, 564–582.

Lal, R (2005) "World crop residues production and implications of its use as a biofuel" *Environment International*, *31*, (4): 575–584.

Larson, ED (2008) "Biofuel production technologies: status, prospects and implications for trade and development" in: United Nations Conference on Trade, Development New York, and Geneva.

Larson, ED and Initiative, UB (2008) “Biofuel production technologies: status, prospects and implications for trade and development”.

Leach, F, Kalghatgi, G, Stone, R and Miles, P (2020) “The scope for improving the efficiency and environmental impact of internal combustion engines” *Transportation Engineering*, *1*, 100005.

Leal, MRL, Galdos, MV, Scarpare, FV, Seabra, JE, Walter, A and Oliveira, CO (2013) “Sugarcane straw availability, quality, recovery and energy use: a literature review” *Biomass and Bioenergy*, *53*, 11–19.

Liguori, R, Ventorino, V, Pepe, O and Faraco, V (2016) “Bioreactors for lignocellulose conversion into fermentable sugars for production of high added value products” *Applied microbiology and biotechnology*, *100*, 597–611.

Liska, AJ and Cassman, KG (2008) “Towards standardization of life-cycle metrics for biofuels: Greenhouse gas emissions mitigation and net energy yield” *Journal of Biobased Materials and Bioenergy*, *2*, (3): 187–203.

Liu, D and Ma, F (2011) “Soybean phospholipids”, in: *Recent trends for enhancing the diversity and quality of soybean products*, IntechOpen.

Living History Farms (2023) *Soybeans* URL: `https://www.lhf.org/learning-fields/crops/soybeans/` (visited on 11/30/2023).

Loh, Y, Sujan, D, Rahman, ME and Das, CA (2013) “Sugarcane bagasse—The future composite material: A literature review” *Resources, Conservation and Recycling*, *75*, 14–22.

Lopes, ES, Rivera, EC, Jesus Gariboti, JC de, Feistel, LHZ, Dutra, JV, Maciel Filho, R and Tovar, LP (2020) “Kinetic insights into the lignocellulosic biomass-based levulinic acid production by a mechanistic model” *Cellulose*, *27*, 5641–5663.

Luis, P and Van der Bruggen, B (2014) “Exergy analysis of energy-intensive production processes: advancing towards a sustainable chemical industry” *Journal of Chemical Technology & Biotechnology*, *89*, (9): 1288–1303.

Macedo, IC, Seabra, JE and Silva, JE (2008) “Green house gases emissions in the production and use of ethanol from sugarcane in Brazil: the 2005/2006 averages and a prediction for 2020” *Biomass and bioenergy*, *32*, (7): 582–595.

Martelli-Tosi, M, Assis, OB, Silva, NC, Esposto, BS, Martins, MA and Tapia-Blácido, DR (2017) “Chemical treatment and characterization of soybean straw and soybean protein isolate/straw composite films” *Carbohydrate polymers*, *157*, 512–520.

Medic, J, Atkinson, C and Hurburgh, CR (2014) “Current knowledge in soybean composition” *Journal of the American oil chemists’ society*, *91*, 363–384.

Meira, M, Quintella, C, Ribeiro, E, Silva, H and Guimarães, A (2015) “Overview of the challenges in the production of biodiesel” *Biomass Conversion and Biorefinery*, *5*, 321–329.

Menandro, LMS, Cantarella, H, Franco, HCJ, Kölln, OT, Pimenta, MTB, Sanches, GM, Rabelo, SC and Carvalho, JLN (2017) “Comprehensive assessment of sugarcane straw: implications for biomass and bioenergy production” *Biofuels, Bioproducts and Biorefining*, *11*, (3): 488–504.

Merckel, RD, Labuschagne, FJ and Heydenrych, MD (2020) “Energy metrics of fuel juxtaposed with mass yield metrics” *Renewable Energy*, *159*, 371–379.

Merckel, RD *et al* (2019) “The impact of oxygen exothermicity on energy quality of biofuels and catalytic upgrading” phdthesis, University of Pretoria.

Merckel, RD, Labuschagne, FJWJ and Heydenrych, M (2019) “Oxygen consumption as the definitive factor in predicting heat of combustion” *Applied energy*, *235*, 1041–1047.

Michailos, SE and Webb, C (2019) “Biorefinery approach for ethanol production from bagasse”, in: *Bioethanol production from food crops*, Elsevier: pp. 319–342.

Microsoft Corporation (July 1, 2024) *Microsoft Excel* version 2019 (16.0) URL: `https://office.microsoft.com/excel`.

Modesto, M, Zemp, RJ and Nebra, SA (2009) “Ethanol production from sugar cane: assessing the possibilities of improving energy efficiency through exergetic cost analysis” *Heat Transfer Engineering*, *30*, (4): 272–281.

Morais, S, Martins, A and Mata, TM (2010) "Comparison of allocation approaches in soybean biodiesel life cycle assessment" *Journal of the Energy Institute*, *83*, (1): 48–55.

Morris, M, Waldheim, L, *et al* (2001) "Biomass power generation: sugar cane bagasse and trash." in: *International Society of Sugar Cane Technologists. Proceedings of the XXIV Congress, Brisbane, Australia, 17-21 September 2001. Volume 1* Australian Society of Sugar Cane Technologists: pp. 272–274.

Motghare, KA, Rathod, AP, Wasewar, KL and Labhsetwar, NK (2016) "Comparative study of different waste biomass for energy application" *Waste management*, *47*, 40–45.

Mourad, AL and Walter, A (2011) "The energy balance of soybean biodiesel in Brazil: a case study" *Biofuels, Bioproducts and Biorefining*, *5*, (2): 185–197.

Muhaji and Sutjahjo, D (2018) "The characteristics of bioethanol fuel made of vegetable raw materials" in: *IOP Conference Series: Materials Science and Engineering* vol. 296 IOP Publishing: p. 012019.

Myint, LL and El-Halwagi, MM (2009) "Process analysis and optimization of biodiesel production from soybean oil" *Clean Technologies and Environmental Policy*, *11*, 263–276.

Naik, SN, Goud, VV, Rout, PK and Dalai, AK (2010) "Production of first and second generation biofuels: a comprehensive review" *Renewable and sustainable energy reviews*, *14*, (2): 578–597.

Nasir, N, Daud, WRW, Kamarudin, S and Yaakob, Z (2013) "Process system engineering in biodiesel production: A review" *Renewable and Sustainable Energy Reviews*, *22*, 631–639.

Niphadkar, S, Bagade, P and Ahmed, S (2018) "Bioethanol production: insight into past, present and future perspectives" *Biofuels*, *9*, (2): 229–238.

Oliveira, FM, Pinheiro, IO, Souto-Maior, AM, Martin, C, Gonçalves, AR and Rocha, GJ (2013) "Industrial-scale steam explosion pretreatment of sugarcane straw for enzymatic hydrolysis of cellulose for production of second generation ethanol and value-added products" *Bioresource technology*, *130*, 168–173.

Oliveira, LR, Nascimento, VM, Goncalves, AR and Rocha, GJ (2014) “Combined process system for the production of bioethanol from sugarcane straw” *Industrial Crops and Products*, *58*, 1–7.

Oliveira, T, Cardoso, C and Ataide, C (2015) “Fast pyrolysis of soybean hulls: analysis of bio-oil produced in a fluidized bed reactor and of vapor obtained in analytical pyrolysis” *Journal of Thermal Analysis and Calorimetry*, *120*, 427–438.

Ortiz, PS and Oliveira Jr, S de (2014) “Exergy analysis of pretreatment processes of bioethanol production based on sugarcane bagasse” *Energy*, *76*, 130–138.

Ozyuguran, A, Akturk, A and Yaman, S (2018) “Optimal use of condensed parameters of ultimate analysis to predict the calorific value of biomass” *Fuel*, *214*, 640–646.

Panthee, D, Pantalone, V and Saxton, A (2006) “Modifier QTL for fatty acid composition in soybean oil” *Euphytica*, *152*, 67–73.

Parmar, K (2017) “Biomass-An overview on composition characteristics and properties” *IRA-International journal of applied sciences*, *7*, (1): 42–51.

Patzek, TW (2009) “A first law thermodynamic analysis of biodiesel production from soybean” *Bulletin of Science, Technology & Society*, *29*, (3): 194–204.

Pereira, SC, Maehara, L, Machado, CMM and Farinas, CS (2015) “2G ethanol from the whole sugarcane lignocellulosic biomass” *Biotechnology for biofuels*, *8*, (1): 1–16.

Persson, T, Garcia, AG y, Paz, JO, Jones, JW and Hoogenboom, G (2009) “Net energy value of maize ethanol as a response to different climate and soil conditions in the southeastern USA” *Biomass and Bioenergy*, *33*, (8): 1055–1064.

Petersen, AM, Aneke, MC and Görgens, JF (2014) “Techno-economic comparison of ethanol and electricity coproduction schemes from sugarcane residues at existing sugar mills in Southern Africa” *Biotechnology for Biofuels*, *7*, 1–19.

Petersen, AM, Van der Westhuizen, WA, Mandegari, MA and Görgens, JF (2018) “Economic analysis of bioethanol and electricity production from sugarcane in South Africa” *Biofuels, Bioproducts and Biorefining*, *12*, (2): 224–238.

Phuttaro, C, Sawatdeenarunat, C, Surendra, K, Boonsawang, P, Chaiprapat, S and Khanal, SK (2019) "Anaerobic digestion of hydrothermally-pretreated lignocellulosic biomass: Influence of pretreatment temperatures, inhibitors and soluble organics on methane yield" *Bioresource technology*, *284*, 128–138.

Pimentel, D and Patzek, TW (2005) "Ethanol production using corn, switchgrass, and wood; biodiesel production using soybean and sunflower" *Natural resources research*, *14*, 65–76.

Pippo, WA, Luengo, CA, Alberteris, LAM, Garzone, P and Cornacchia, G (2011) "Energy recovery from sugarcane-trash in the light of 2nd generation biofuels. Part 1: current situation and environmental aspects" *Waste and Biomass Valorization*, *2*, (1): 1–16.

Pradhan, A, Shrestha, D, McAloon, A, Yee, W, Haas, M, Duffield, J and Shapouri, H (2009) *Energy life-cycle assessment of soybean biodiesel* tech. rep.

Pradhan, A, Shrestha, D, McAloon, A, Yee, W, Haas, M and Duffield, J (2011) "Energy life-cycle assessment of soybean biodiesel revisited" *Transactions of the ASABE*, *54*, (3): 1031–1039.

Pradhan, A, Shrestha, DS, Van Gerpen, J and Duffield, J (2008) "The energy balance of soybean oil biodiesel production: a review of past studies" *Transactions of the ASABE*, *51*, (1): 185–194.

Priolli, RHG, Campos, J, Stabellini, N, Pinheiro, JB and Vello, NA (2015) "Association mapping of oil content and fatty acid components in soybean" *Euphytica*, *203*, 83–96.

PubChem (2023a) *Beta-Sitosterol* URL: `https://pubchem.ncbi.nlm.nih.gov/compound/Beta-Sitosterol` (visited on 09/15/2023).

PubChem (2023b) *Linoleic Acid* URL: `https://pubchem.ncbi.nlm.nih.gov/compound/Linoleic-Acid` (visited on 09/15/2023).

PubChem (2023c) *Linolein* URL: `https://pubchem.ncbi.nlm.nih.gov/compound/Linolein` (visited on 09/15/2023).

Rajaeifar, MA, Ghobadian, B, Safa, M and Heidari, MD (2014) "Energy life-cycle assessment and CO2 emissions analysis of soybean-based biodiesel: a case study" *Journal of Cleaner Production*, *66*, 233–241.

Raugei, M, Rugani, B, Benetto, E and Ingwersen, WW (2014) "Integrating emergy into LCA: potential added value and lingering obstacles" *Ecological Modelling*, *271*, 4–9.

Renewable Fuels Association (2023) *Annual World Fuel Ethanol Production* URL: `https://ethanolrfa.org/markets-and-statistics/annual-ethanol-production` (visited on 05/05/2024).

Rincón, L, Jaramillo, J and Cardona, C (2014) "Comparison of feedstocks and technologies for biodiesel production: An environmental and techno-economic evaluation" *Renewable Energy*, *69*, 479–487.

Rocha, GJ, Martín, C, Silva, VF da, Gómez, EO and Gonçalves, AR (2012) "Mass balance of pilot-scale pretreatment of sugarcane bagasse by steam explosion followed by alkaline delignification" *Bioresource technology*, *111*, 447–452.

Rocha, GdM, Gonçalves, AR, Oliveira, B, Olivares, E and Rossell, C (2012) "Steam explosion pretreatment reproduction and alkaline delignification reactions performed on a pilot scale with sugarcane bagasse for bioethanol production" *Industrial Crops and Products*, *35*, (1): 274–279.

Rodriguez, RdG, Scanlon, BR, King, CW, Scarpare, FV, Xavier, AC and Pruski, FF (2018) "Biofuel-water-land nexus in the last agricultural frontier region of the Brazilian Cerrado" *Applied Energy*, *231*, 1330–1345.

Romero, JC and Linares, P (2014) "Exergy as a global energy sustainability indicator. A review of the state of the art" *Renewable and Sustainable Energy Reviews*, *33*, 427–442.

Rosen, MA (2018) "Environmental sustainability tools in the biofuel industry" *Biofuel Research Journal*, *5*, (1): 751–752.

Saladini, F, Patrizi, N, Pulselli, FM, Marchettini, N and Bastianoni, S (2016) "Guidelines for emergy evaluation of first, second and third generation biofuels" *Renewable and Sustainable Energy Reviews*, *66*, 221–227.

Salvi, B and Panwar, N (2012) "Biodiesel resources and production technologies–A review" *Renewable and sustainable energy reviews*, *16*, (6): 3680–3689.

Sartori, MMP, Oliveira Florentino, H de, Basta, C and Leão, AL (2001) "Determination of the optimal quantity of crop residues for energy in sugarcane crop management using linear programming in variety selection and planting strategy" *Energy*, *26*, (11): 1031–1040.

Selvaraj, R, Praveenkumar, R and Moorthy, IG (2019) "A comprehensive review of biodiesel production methods from various feedstocks" *Biofuels*, *10*, (3): 325–333.

Şensöz, S and Kaynar, İ (2006) "Bio-oil production from soybean (Glycine max L.); fuel properties of Bio-oil" *Industrial Crops and Products*, *23*, (1): 99–105.

Shahbeig, H, Shafizadeh, A, Rosen, MA and Sels, BF (2022) "Exergy sustainability analysis of biomass gasification: a critical review" *Biofuel Research Journal*, *9*, (1): 1592–1607.

Sheehan, J, Camobreco, V, Duffield, J, Graboski, M and Shapouri, H (1998) *Life cycle inventory of biodiesel and petroleum diesel for use in an urban bus. Final report* tech. rep. National Renewable Energy Lab.(NREL), Golden, CO (United States).

Silva Ortiz, PA, Maciel Filho, R and Posada, J (2019) "Mass and heat integration in ethanol production mills for enhanced process efficiency and exergy-based renewability performance" *Processes*, *7*, (10): 670.

Smith, JM (1950) *Introduction to chemical engineering thermodynamics*.

Soccol, CR, de Souza Vandenberghe, LP, Medeiros, ABP, Karp, SG, Buckeridge, M, Ramos, LP, Pitarelo, AP, Ferreira-Leitão, V, Gottschalk, LMF, Ferrara, MA, *et al* (2010) "Bioethanol from lignocelluloses: status and perspectives in Brazil" *Bioresource technology*, *101*, (13): 4820–4825.

Souza, SP, Seabra, JE and Nogueira, LAH (2018) "Feedstocks for biodiesel production: Brazilian and global perspectives" *Biofuels*, *9*, (4): 455–478.

Statista (2023) *Combined nameplate capacity of biodiesel and renewable diesel refineries in major producing countries worldwide from 2019 to 2023* URL: `https://www.statista.com/statistics/1445877/global-biodiesel-refineries-capacity/#:~:text=Biodiesel%20and%20renewable%20diesel%20refineries,in%20the%20period%20of%20consideration.` (visited on 05/05/2024).

Technical Committee ISO/TC 207, EM (2006) *Environmental management-life cycle assessment-principles and framework*, International Organization for Standardization.

Tian, Y, Wang, F, Djandja, JO, Zhang, SL, Xu, YP and Duan, PG (2020) "Hydrothermal liquefaction of crop straws: Effect of feedstock composition" *Fuel*, *265*, 116946.

Tsiropoulos, I, Faaij, AP, Seabra, JE, Lundquist, L, Schenker, U, Briois, JF and Patel, MK (2014) "Life cycle assessment of sugarcane ethanol production in India in comparison to Brazil" *The International Journal of Life Cycle Assessment*, *19*, 1049–1067.

Van Rossum, G and Drake, FL (2009) *Python 3 Reference Manual*, CreateSpace, Scotts Valley, CA ISBN: 1441412697.

Velásquez-Arredondo, HI, Junior, SDO and Benjumea, P (2012) "Exergy efficiency analysis of chemical and biochemical stages involved in liquid biofuels production processes" *Energy*, *41*, (1): 138–145.

Velásquez-Arredondo, HI, Ruiz-Colorado, A, *et al* (2010) "Ethanol production process from banana fruit and its lignocellulosic residues: energy analysis" *Energy*, *35*, (7): 3081–3087.

Verma, P and Sharma, M (2016) "Review of process parameters for biodiesel production from different feedstocks" *Renewable and sustainable energy reviews*, *62*, 1063–1071.

Von Blottnitz, H and Curran, MA (2007) "A review of assessments conducted on bio-ethanol as a transportation fuel from a net energy, greenhouse gas, and environmental life cycle perspective" *Journal of cleaner production*, *15*, (7): 607–619.

Walter, A and Ensinas, AV (2010) "Combined production of second-generation biofuels and electricity from sugarcane residues" *Energy*, *35*, (2): 874–879.

Wang, M (2008) "The greenhouse gases, regulated emissions, and energy use in transportation (GREET) model: Version 1.5" *Center for Transportation Research, Argonne National Laboratory*,

Wang, Q, Wang, E, Li, K, Husnain, N and Li, D (2020) "Synergistic effects and kinetics analysis of biochar with semi-coke during CO2 co-gasification" *Energy*, *191*, 116528.

Williamson, S, Lukic, M and Emadi, A (2006) "Comprehensive drive train efficiency analysis of hybrid electric and fuel cell vehicles based on motor-controller efficiency modeling" *IEEE Transactions on power electronics*, *21*, (3): 730–740.

Wyman, CE, Decker, SR, Himmel, ME, Brady, JW, Skopec, CE and Viikari, L (2005) “Hydrolysis of cellulose and hemicellulose” *Polysaccharides: Structural diversity and functional versatility*, *1*, 1023–1062.

Zhang, Y, Dube, M, McLean, D and Kates, M (2003) “Biodiesel production from waste cooking oil: 1. Process design and technological assessment” *Bioresource technology*, *89*, (1): 1–16.

Zhao, X, Moates, G, Wilson, D, Ghogare, R, Coleman, M and Waldron, K (2015) “Steam explosion pretreatment and enzymatic saccharification of duckweed (Lemna minor) biomass” *Biomass and Bioenergy*, *72*, 206–215.

Appendix A: Biodiesel model parameters

All parameters for the biodiesel model are taken from Sheehan *et al* (1998) unless otherwise indicated.

A.1 Mass balance parameters

Table A.1.1: Process parameters for cultivation and harvesting, and soybean oil and meal preparation.

Parameter	Value	Unit
Cultivation & Harvesting		
Straw yield [a]	1.35	kg kg_{beans}^{-1}
Straw left on the field [b]	50	wt. %
Cleaning & drying		
Final moisture in beans	10.50	wt. %
Dehuller		
Meal lost	0.65	wt. %
Oil lost	0.58	wt. %
Hulls recovered	99.00	wt. %
Moisture with hulls	0.74	wt. %
Conditioner		
Final bean moisture	9.00	wt. %

[a] Martelli-Tosi *et al* (2017), Bose & Martins Filho (1984), and Lopes *et al* (2020)

[b] De Pretto, Tardioli & Costa (2017)

Table A.1.2: Process parameters for cultivation and harvesting, and soybean oil and meal preparation (continued).

Parameter	Value	Unit
Oil extraction		
Total hexane used	1.2	kg $\text{kg}_{\text{flaked beans}}^{-1}$
Make-up hexane	0.0024	kg $\text{kg}_{\text{flaked beans}}^{-1}$
Recovered hexane	1.1976	kg $\text{kg}_{\text{flaked beans}}^{-1}$
Oil concentration in miscella	23.50	wt. %
Oil recovered in miscella	96.00	wt. %
Hexane concetration with the flakes	35.00	wt. %
Oil recovery		
Hexane recovery	100.00	wt. %
Oil lost	0.00	wt. %
Solvent recovery		
Hexane recovery	99.80	wt. %
Hull and meal processing		
Meal moisture after toaster	18.00	wt. %
Meal moisture after drying	14.00	wt. %
Meal moisture after cooler	12.00	wt. %
Final hull moisture *	19.00	wt. %

* Assumed based on mass balance by Granjo, Duarte & Oliveira, 2017

Table A.1.3: Process parameters for degumming and alkali refining.

Parameter	Value	Unit
Degumming		
Total oil loss	3.11	wt. %
Oil lost from triglyceride [a]	0.476	wt. %
Oil lost from phosphatides [a]	2.50	wt. %
Oil lost from unsaponifiable matter [a]	0.134	wt. %
Water addition	75	wt. % of phosphatide mass
Water content in gum/oil mixture [b]	5.00	wt. %
Alkali refining		
NaOH stoicheometric excess	113	%
Wash water addition	15	wt. % of oil
Oil lost from FFAs	0.719	wt. %
Oil lost from Triglycerides	1.799	wt. %
Oil lost from Unsaponifiable matter	1.485	wt. %

[a] Calculated

[b] Assumed

Table A.1.4: Process parameters for soybean oil conversion.

Parameter	Value	Unit
Transesterification		
Methanol:oil ratio	6:1	mol mol^{-1}
NaOH [a]	1.0	wt. % of oil
2 Reactant temperature	60	°C
Overall triglyceride conversion	99	wt. %
Aqueous phase carried over to FAME	5.0	wt. %
FAME purification (Overall)		
Ester phase recovered	100	wt. %
Moisture in ester product	0.00	wt. %
Overall aqueous phase recovery	100	wt. %
Glycerol and methanol recovery		
Fist distillation: Glycerol bottoms water content	20	wt. %
Second distillation: methanol in bottoms	0.5	wt. %
Second distillation: water in distillate	0.5	wt. %
Overall glycerol recovery	100	wt. %
Overall methanol recovery	99	wt. %

[a] Myint & El-Halwagi (2009)

A.2 Energy consumption parameters

Table A.2.5: Energy inputs for harvesting and cultivation. *Average of Castanheira* et al *(2015), Pimentel & Patzek (2005), Pradhan, Shrestha, McAloon, Yee, Haas & Duffield (2011), and Sheehan* et al *(1998).*

Utility	Value MJ t_{beans}^{-1}
Diesel	622
Petroleum	253
LPG	21.1
Natural gas	14.3
Electricity	12.7

Table A.2.6: Energy inputs for soybean oil extraction and meal and hull processing.

Component	Electricity MJ t_{beans}^{-1}	Steam MJ t_{beans}^{-1}	Natural gas MJ t_{water}^{-1}	Hexane MJ $t_{flaked\ beans}^{-1}$
Soybean preparation				
Cleaning	-14.33			
Drying	-55.8		-3.489 [a]	
Cracking	-14.90			
Dehulling	-8.50			
Conditioning	-4.07	-173.35		
Flaking	-50.26			
Hexane extraction				
Oil extraction	-12.96			-117.67

[a] Erickson, 2015

Table A.2.7: Energy inputs for soybean oil extraction and meal and hull processing (continued).

Component	Electricity MJ $t_{beans}$$^{-1}$	Steam MJ $t_{beans}$$^{-1}$	Natural gas MJ $t_{water}$$^{-1}$	Hexane MJ $t_{flaked\ beans}$$^{-1}$
Hull and meal processing				
Desolventizer toaster	-14.90	-421.85		
Meal dryer	-2.304	-85.96		
Meal cooler	-9.144			
Meal grinding	-26.064			
Hull grinding	-19.44			
Hull toaster		-48.97		
Oil recovery				
First effect evaporator	-0.54			
Second effect evaporator	-0.54	-41.748		
Third effect evaporator	-0.288	-45.338		
Solvent recovery				
Solvent recovery	-1.872			
Waste treatment	-1.872	-36.811		
Degumming				
Hydration	-0.864	-36.811		
Centrifuge	-2.448			
Dryer	-2.772	-32.397		

Table A.2.8: Energy inputs for degumming and alkali refining.

Component	Electricity MJ t_{beans}^{-1}	Steam MJ t_{beans}^{-1} or MJ $t_{biodiesel}^{-1}$
Degumming		
Hydration	-0.864	-36.028 MJ t_{beans}^{-1}
Centrifuge	-2.448	
Drying	-2.772	-32.397 MJ t_{beans}^{-1}
Alkali refining		
Crude oil heater		-108.515 MJ $t_{biodiesel}^{-1}$
Wash water heater		-32.554 MJ $t_{biodiesel}^{-1}$
Preheater for vacuum dryer		-9.784 MJ $t_{biodiesel}^{-1}$
Vacuum dryer		-4.013 MJ $t_{biodiesel}^{-1}$

Table A.2.9: Energy inputs for oil conversion.

Component	Electricity MJ t_{beans}^{-1}	Steam MJ $t_{biodiesel}^{-1}$
Transesterification		
First reactor		-97.012
Second reactor		-10.119
FAME purification		
Wash water heater		-41.914
Ester heater		-104.786
Preheater for vacuum dryer		-83.848
Vacuum dryer		-2.285
Glycerol recovery		
Glycerine preheater		-75.591
Distillation reboiler		-57.264
Methanol recovery		
Methanol dryer		-224.580

Appendix B: Bioethanol model parameters

B.1 Mass and energy balance parameters

Table B.1.1: Process parameters for cultivation and harvesting, and 1G bioethanol production.

Parameter	Value	Unit
Cultivation and Harvesting		
Fossil fuel energy consumption	-139	MJ t_{cane}^{-1}
Sugarcane straw produced (dry) [c]	140	kg t_{cane}^{-1}
Straw moisture [c, g]	15	wt. %
Straw recovered from the field [a]	50	wt. %
Cleaning		
Dirt removed	90	wt. %
Milling		
Bagasse yield (wet)	240	kg t_{cane}^{-1}
Bagasse moisture content [a, b]	50	wt. %
Sugar recovery [i]	97	wt. %
Water for imbibition [e]	0.28	t t_{cane}^{-1}
Electricity consumption	16 [f]	kWh t_{cane}^{-1}
Pre-treatment		
Preheating steam consumption (2.5 bar) [d]	70.25	kg t_{cane}^{-1}
CaO concentration [a]	10	wt. %
CaO flowrate [a]	2	kg t_{juice}^{-1}
Steam consumption (2.5 bar) after liming [d]	68.49	kg t_{cane}^{-1}
Sugar recovery after juice treatment [c]	99.5	wt. %
Clarified juice sugar concentration [f]	15	wt. %

Table B.1.2: Process parameters for cultivation and harvesting, and 1G bioethanol production (continued).

Parameter	Value	Unit
Evaporation and sterilisation		
Steam consumption (2.5 bar) for evaporation [d]	114.14	kg t_{cane}^{-1}
Sucrose concentration after evaporation [f]	22	wt. %
Steam consumption (2.5 bar) for sterilisation [d]	32.14	kg t_{cane}^{-1}
Fermentation		
Sucrose to glucose mass yield [*]	100	wt. %
Glucose to ethanol mass yield [f]	90.48	wt. %
Distillation and dehydration		
Hydrous ethanol concentration [e]	93	wt. %
Steam consumption (2.5 bar) for azeotropic distillation [c]	1.5	kg L^{-1}_{EtOH}
Anhydrous ethanol concentration [e]	99.6	wt. %
Steam consumption (2.5 bar) for dehydration [h]	0.6	kg L^{-1}_{EtOH}
Overall ethanol recovery [c]	99.7	wt. %
Density of bioethanol [j]	789	kg m^{-3}
Auxiliary operations		
Electricity consumption [c]	-30	kWh t_{cane}^{-1}

[*] Assumed

[a] Furlan, Tonon Filho, *et al* (2013)

[b] Carvalho *et al* (2020)

[c] Dias, Cunha, Jesus, Rocha, *et al* (2011)

[d] Dias, Modesto, *et al* (2011)

[e] Dias, Junqueira, Cavalett, Pavanello, *et al* (2013)

[f] Dias, Ensinas, *et al* (2009)

[g] Oliveira, Pinheiro, *et al* (2013)

[h] Dias, Junqueira, Cavalett, Cunha, Jesus, Rossell, *et al* (2012)

[i] Modesto, Zemp & Nebra (2009)

[j] Muhaji & Sutjahjo (2018)

Table B.1.3: Process parameters for 2G bioethanol production.

Parameter	Value	Unit
Steam Explosion Pretreatment		
Steam pressure [a]	1.25	MPa
Steam temperature [a]	190	°C
Steam consumption [a]	0.55	kg $\mathrm{kg_{LM,\ AR}}^{-1}$
Hemicellulose hydrolysis [a, b]	70	wt. %
Cellulose hydrolysis [c]	70	wt. %
Lignin solubilisation [b]	0.00	wt. %
Xylose fermentation		
Xylose to ethanol conversion [b]	80	wt. %
Alkaline delignification		
Lignin solubilisation [d]	92.7	wt. %
Enzymatic hydrolysis		
Cellulose hydrolysis [c]	80	wt. %
Hemicellulose hydrolysis [c]	80	wt. %
Filters		
Solids recovery [c]	99.5	wt. %
Soluble solids loss [c]	10	wt. %
Auxiliary operations		
Electricity consumption [b]	-24	kWh $\mathrm{t_{LM,\ AR}}^{-1}$

LM, AR: Lignocellulose material on an as received basis

[a] Ortiz & Oliveira Jr (2014)

[b] Dias, Junqueira, Cavalett, Cunha, Jesus, Rossell, *et al* (2012)

[c] Dias, Junqueira, Rossell, *et al* (2013)

[d] Rocha, Gonçalves, *et al* (2012)

Appendix C: The process model calculations

The process models for sugarcane-bioethanol and soybean-biodiesel were developed in Microsoft Excel and Python. The files can be accessed using the following link:

Click here for the process models and calculations