

Process integration, economic and environmental analysis tools for biorefinery design

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List of Abbreviations

A	Plant Age
AAR	Annual average rainfall
AP	Acidification Potential
ARU	Abiotic Resources Use
AX	Arabinoxylan
C	Economic cost (of feedstock, utility, etc.)
C ₅	Five carbons, e.g. xylose (C ₅ H ₁₂ O ₅) is a C ₅ sugar
C ₆	Six carbons, e.g. glucose (C ₆ H ₁₂ O ₆) is a C ₆ sugar
CEPCI	Chemical Engineering Plant Cost Index
CFG	Centrifugation/Centrifuge
CHP	Combined Heat and Power
COP	Cost of Production
CPE	Cumulative Fossil Primary Energy Demand
CVP	(environmental impact) Credit Value on Processing
DCC	(bioethanol) Demand Composite Curve
DDGS	Distiller's Dried Grains with Solubles
DM	Dry matter
DOE	Department of Energy (US)
EI	Environmental Impact
EIA	Energy Information Administration (US)

EP	Eutrophication Potential
eq	equivalents
E_{ratio}	Energy ratio (energy output / CPE)
EU	European Union
EV	Economic value
EVEI	Economic Value and Environmental Impact
F&P	Fertilisers and Pesticides
FAME	Fatty Acid Methyl Esters
FAO	Food and Agriculture Organisation of the United Nations
FE	(agricultural) Field Emissions
FFA	Free Fatty Acids
FO	(agricultural) Field Operations
GC	Grain Conditioning
GHG	Greenhouse Gas
GWP_{100}	Global Warming Potential in a 100-year horizon
HHV	Higher Heating Value
HP	High Pressure (steam)
HRSG	High Recovery Steam Generator (heat exchanger)
I	Environmental impact cost (embodied EI of feedstock, utility, etc.)
IBGCC	Integrated Biomass Gasification and Combined Cycle
IBGCC-H ₂	IBGCC with hydrogen production

IBGCC-MeOH	IBGCC with methanol production
IC	Impact Categories
ICP	(environmental) Impact Cost of Production
IEA	International Energy Agency
IO	Environmental Impact from unit operation
IPCC	Intergovernmental Panel on Climate Change
ISO	International Organisation for Standardisation
K	Potassium (fertiliser)
LCA	Life cycle assessment/analysis
LCI	Life cycle inventories
LHV	Lower Heating Value
LP	Low Pressure (steam)
LPG	Liquefied Petroleum Gas
M	Million or 1×10^6 (e.g. M£ = 1 million £ = 1×10^6 £)
MP	Medium Pressure (steam)
N	Nitrogen or Nitrogen fertilisation rate
NG	Natural gas
NREL	National Renewable Energy Laboratories (US)
O	Operating Cost
OECD	Organisation for Economic Co-operation and Development
P	Phosphorous (fertiliser)

PEN	Product Exchange Network
PPU	Precipitation Unit
PSA	Pressure Swing Adsorption
RDY	Rotary Dryer
SCC	(bioethanol) Source Composite Curve
ST	Steam turbine
TG	Tryglycerides
TMU	Treatment Unit
UF	Ultrafiltration
UFOP	Union zur Förderung von Oel- und Proteinpflanzen
UK	United Kingdom
UNIFAC	UNIQUAC Functional-group Activity Coefficients
US	United States
VBA [®]	Visual Basic for Applications
VHP	Very High Pressure (steam)
VOP	(economic) Value on Processing
WGSR	Water Gas Shift Reactor
WSU	Washing and Sieving Unit
WWT	Wastewater Treatment
Δe	Economic margin
Δi	EI saving margin

ABSTRACT

Process integration, economic and environmental analysis tools for biorefinery design

Renewability and the carbonaceous basis of biomass provide potential for both energy and chemical production in biorefineries in a fashion similar to crude oil refineries. Biorefineries are envisaged as having a key role in the transition to a more sustainable industry, especially as a means to mitigate greenhouse gas (GHG) emissions. A biorefinery is a concept for the flexible, efficient, cost-effective and sustainable conversion of biomass through a combination of process technologies into multiple products. This implies that biorefineries must be integrated through designs that exploit the interactions between material and energy streams.

The wide range of possibilities for biomass feedstock, processes and products poses a challenge to biorefinery design. Integrating biorefineries within evolving economic and environmental policy contexts requires careful analysis of the configurations to be deployed from early in the design stage. This research therefore focuses on the application and development of methodologies for biorefinery design encompassing process integration tools, economic and environmental sustainability analyses together. The research is presented in the form of papers published or submitted to relevant peer-reviewed journals, with a preamble for each paper and a final synthesis of the work as a whole.

In a first stage, mass pinch analysis was adapted into a method for integration of biorefineries producing bioethanol as a final product and also utilising bioethanol as a working fluid within the biorefinery. The tool allows targeting minimum bioethanol utilisation and assessing network modifications to diminish revenue losses. This new application could stimulate the emergence of similar approaches for the design of integrated biorefineries. The thesis then moves to combine feedstock production models, process simulations in Aspen Plus[®] and process integration with LCA, to improve energy efficiency and reduce GHG emissions of biorefineries. This work, presented via two publications covering wheat to bioethanol and Jatropha to biodiesel or green diesel, provided evidence of the benefits of biorefinery integration for energy saving and climate change adaptation.

The multilevel modelling approach is then further integrated into a methodology developed for the combined evaluation of the economic potential and GHG emissions saving of a biorefinery from the marginal performances of biorefinery products. The tool allows assessing process integration pathways and targeting for policy compliance. The tool is presented via two further publications, the first drawing analogies between value analysis and environmental impact analysis in order to create the combined Economic Value and Environmental Impact (EVEI) analysis methodology, the second extending this to demonstrate how the tool can guide judicious movement of environmental burdens to meet policy targets.

The research embodied in this thesis forms a systematic basis for the analysis and generation of biorefinery process designs for enhanced sustainability. The tools presented will facilitate both the implementation of integrated biorefinery designs and the cultivation of a community of biorefinery engineers for whom such integrated thinking is their distinctive and defining attribute.

DECLARATION

I declare that no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

The thesis contains original papers published in peer-reviewed journals (Publication 1, 2 and 4) and unpublished / submitted papers (Publications 3 and 5). I confirm that the materials covered in Publications 1 to 5 in the thesis, including simulation models, data, calculations, analysis are the results of my own original contribution. These studies were carried out under the supervision of the co-authors of the research papers, Dr. Jhuma Sadhukhan and Dr. Grant Campbell. The contribution of these co-authors was through the provision of technical guidance and language corrections in all the publications presented. Dr. Matthew Leach and Dr. Philipp Sinclair have also provided technical advice on the quality and significance of the research in Publication 2 and Publication 5. Mr. Muhammad H. Ibrahim and Dr. Jorge Martinez-Herrera have kindly supported with essential data input for the studies presented in Publication 2 and Publication 3, respectively. I certify that I have obtained permission from the co-authors for incorporating the published materials in my thesis.

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All the work presented in this thesis has been completed whilst a registered student at The University of Manchester.

I confirm that this is a true statement and that, subject to any comments above, the submission is my own original work.

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Elias

Chapter 1

Introduction

1.1 Biorefineries as a key for a sustainable development

Coal, crude oil and natural gas have been the predominant sources of energy, organic chemicals and materials at different times since the 18th century. Today, in the crude oil era, the political instability in the region with the highest reserves in the world – the Middle East – combined with inevitable depletion and forecasted price increases (crude oil price projected as 150 \$/barrel in 2035; EIA, 2013) is causing uncertainty in future supplies. There is also a desire of countries for less dependency on other countries' resources to supply their increasing demands of energy and goods. In addition, the planet Earth is experiencing an imbalance of energy with a flow of energy absorbed 0.5 PW (1 PW=10¹⁵ W) higher than the energy emitted back to the universe. This excess energy remains in the planet due to high concentration of greenhouse gases (GHG) in the atmosphere, mainly CO₂, CH₄ and N₂O, creating a global warming effect – the driving force for climate change (Kravanja, 2012). It is now recognised that those GHG are mainly produced from agricultural and industrial activities thus creating a link between current economic development, climate change and the energy balance of the planet. In addition, the extensive use of fossil resources for current economic development has also produced detrimental effects on air, water and soil affecting all forms of life in the ecosystems.

The political, economic and environmental embattlements faced by current society make the searching for alternatives that can be made commercially available and sustainable a need of utmost urgency. Economies highly dependent on imported fossil resources such as the US and European countries (with an average 53.8% of dependency on imports; Europe's Energy Portal, 2012) are already turning their sights to wind, solar, tidal, hydroelectric, geothermal and biomass energy. Although these renewable sources could supply between 17% and 29% of the world energy demand by 2030 (Peter and Lehmann, 2011), a source of carbon as feedstock for the

supply of chemicals and materials is also required. To address this need, the world is looking back to the past towards the use of biomass – organic material from recent biological origin (plants, animal wastes, algae, etc.). Biomass has not only been humankind's very first source of energy, but has been also used since the first world civilizations such as the Chinese, Egyptians, Persians, Aztecs and Mayans as a source of materials, remedies and other useful products.

Today, biomass is the most important single source of renewable energy providing over 9% of the global total primary energy supply for cooking and heating, particularly in households in developing countries (FAO, 2012). But biomass can also serve as source of functionalised organic chemicals and materials. Biomass is essentially made up of the same chemical elements (carbon, hydrogen and oxygen) as crude oil in varying proportions (Kamm and Kamm, 2005; Luguel, 2008; Demirbas, 2009). This opens the possibility to produce biomass-based products that could directly replace existing crude oil derivatives that are chemically identical (e.g. ethylene from bioethanol can replace ethylene from natural gas) or could substitute those having similar functionality (e.g. polylactic acid can substitute polyethylene terephthalate for plastic bottles) (Kamm and Kamm, 2005; Cherubini et al, 2009). The potential as a source of both energy and chemical makes biomass suitable for the shift from fossil to renewable energy and feedstocks (Wellisch et al., 2010).

Before biomass can be an important source of modern daily life products, there are still issues to solve. While crude oil is a readily transportable fluid extracted from wells and the technology for its processing is advanced, biomass has to be grown and harvested from fields (in the case of crops) or collected (waste vegetable oil, animal manure, other residues) from distributed locations and it is often a low density, high moisture and low calorific value solid material (Wellisch et al., 2010). Besides, the complex chemical structure of biomass, mainly formed by polymeric carbohydrates, lignin and proteins, makes it difficult to access more useful components like C₆ and C₅ sugars which require new process technologies to be developed (Kamm and Kamm, 2005; Luguel, 2008; Demirbas, 2009; King, 2010). The nature and properties of biomass complicate its transportation and processing into useful derivatives and lead to conversion inefficiencies. In turn, these inefficiencies translate into economical disadvantages for the biomass products such

as biofuels which often require government subsidies to be competitive with crude oil products.

There are other issues regarding sustainability: GHG emissions, land use change and the *food vs fuel* dilemma. Biomass from plants can be made available in a cyclic basis within a short period of time and captures CO₂ from the air for photosynthesis. These two characteristics initially created the perception that biomass and its products were inherently sustainable, especially when used for biofuel production. More thoughtful analysis from a life cycle perspective showed the idea to be misleading, as fossil-based inputs, such as diesel, electricity, fertiliser and pesticides, are needed during cultivation and processing. This creates an additional demand of fossil resources and releases of CO₂ and other emissions. For example, nitrogen fertilisers volatilise in the form of N₂O, a GHG with a global warming potential 298 times that of CO₂ (Forster et al., 2007). The inefficient conversion processes create organic wastes that are sent to landfills where methane is produced, another GHG with a global warming potential 25 times that of CO₂ (Forster et al., 2007). The clearing of lands also create the release of the carbon stocked in biomass and soil – the land use change effect, which adds more CO₂ to the carbon cycle. In addition, the diversion of food crops for biofuel (the *food vs fuel* dilemma) and other products represents an issue for the societal viability of biorefineries (Searchinger et al., 2008). The aforementioned disadvantages undermine the economic feasibility and sustainability of biomass processing as an alternative to fossil-based production.

The vision for biomass conversion into a portfolio of energy, fuels, chemicals, polymers, pharmaceuticals, food and fertilisers in a way similar to crude oil refining led to the concept of integrated biorefineries (Kamm and Kamm, 2005; Kamm et al., 2006). By producing a mix of products through flexible and efficient processes, biorefineries have the potential to make biomass processing profitable and sustainable. Biorefineries have recently attracted both academic and industrial interest. The projected market created throughout the entire value chain is \$295 billion by 2020 (King, 2010). Research projects in the EU, US and other countries are making efforts for the establishment of biorefineries through pilot plant demonstrations (US DOE, 2012; Star-Colibri, 2012). Companies already producing biomass derivatives include DuPont (1,3-propanediol and biobutanol), NatureWorks

(polylactic acid), Novozymes (enzymes), BP (biobutanol), Glycos Biotechnology (acetone, ethanol and isoprene), while many others have been projected (BIOCHEM Project, 2010).

Although biorefinery technologies are still under research, biorefineries can benefit from current technologies such as hydrotreatment or gasification to get access to molecules readily adaptable to current infrastructure such as synthetic or green diesel from vegetable oils and syngas from lignocellulosic material (Bridgewater, 2003; Kamm et al., 2006; Huber and Avelino, 2007; Demirbas, 2009; King, 2010). Biotechnological advances for high yield and direct biochemical conversion of biomass into products will also help the development of biorefineries. Biochemical conversions usually require milder process conditions and less conversion steps than petrochemical synthesis routes (Koutinas et al., 2003; Kamm and Kamm, 2005, Kamm et al., 2006). These advantages translate into cheaper construction materials and better process safety management. In terms of sustainability, the substitution of fossil fuels by biomass fuels to supply energy to cultivation and processing contribute to save non-renewable energy and reduce GHG emissions. Even more, animal feed can be co-produced and components such as protein, vitamins and amino acids could be recovered as nutritional additives to improve food quality, addressing in this way the *food vs fuel* dilemma (Dale et al, 2010). Since biorefinery feedstocks have their origin in agriculture, biomass supply chains generate opportunities for rural development. In addition, biorefinery products will be regarded as “green”, “sustainable” or “renewable”, labels that improve the public perception of the chemical industry (Kamm et al., 2006; Wellisch et al., 2010).

The attributes presented above make biorefineries a key element in the transition to a more sustainable energy and chemical industry. However, the exploitation of biomass in biorefineries for energy and chemical supply deserves a more careful assessment regarding efficiency, feasibility and sustainability to ensure the biorefineries really contribute to tackling current societal and environmental concerns. This need is the main motivation for the research presented in this thesis.

1.2 The importance of process integration

The biorefinery concept was developed by analogy to oil refineries (Kamm and Kamm, 2005; Kamm et al., 2006). As shown in **Figure 1.1**, current oil refineries rely on technologies developed throughout decades of history starting from simple production of kerosene via distillation in 1861. Then, the internal combustion engine created a demand for fuels which stimulated the diversification of product portfolio and the development of thermal cracking in 1913 and the fluid catalytic cracking and reforming processes in the 1930s. The valorisation of heavy residuals and heavy crude oils generated technologies such as delayed coking and gasification while more recent concerns about environmental pollution from fuels have driven the development of hydrotreatment and hydrodesulphurisation. The combination of these high throughput technologies allowed converting the whole barrel of crude oil into diverse value-added products including chemical building blocks, while also giving flexibility to adapt to the changing market, which also improved the economics of the refineries (Lynd, 2005, Lynd et al., 2009).

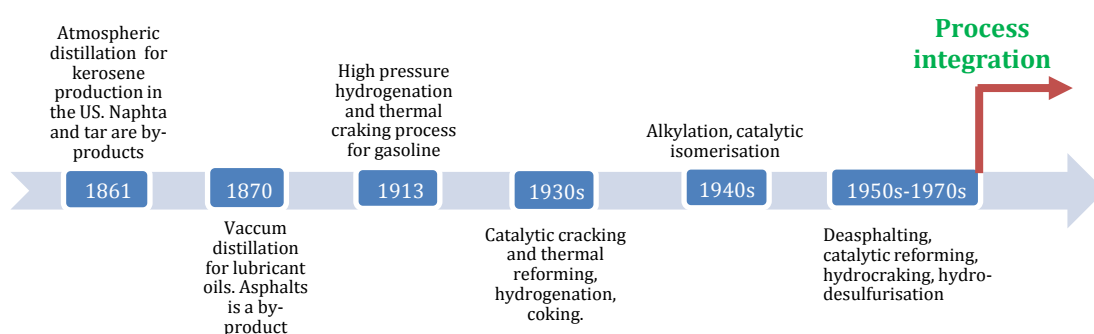


Figure 1.1 Timeline of technology development in crude oil refining and the emergence of process integration (Lynd, 2005).

While simple processes have limited scope for efficiency through process integration, the complexity arising from the combination of the multiple processes in oil refineries gave extensive scope for process integration and the opportunity for the emergence of the first process integration tools during the energy crisis of the 1970s, when energy efficiency became essential. According to Lynd et al. (2009), current highly integrated oil refineries are able to operate typically with 96% efficiency, using only 4% of the available energy content of the crude oil to convert and deliver

that energy into a diverse range of products. The addition of auxiliary energy and material inputs lowers the figure to 70.6%, still a relatively high efficiency.

Research in process integration started in the 1970s (**Figure 1.1**) when the pinch analysis method for the design of heat exchanger networks was developed (Linnhoff and Flower, 1978; Linnhoff and Hindmarsh, 1983). In its early years, pinch analysis caused some scepticism because of the great energy savings of up to 30% reported from the application of a method that use simple concepts rather than complex mathematical equations (Kemp, 2007). Nonetheless, the tool was soon adopted not only by refineries but almost by all process industries. After remarkable success, a research consortium was formed and the world's first Centre for Process Integration was founded in what is now The University of Manchester.

The pinch analysis for heat exchanger networks stimulated the analogous development of mass pinch analysis (El-Hawagi and Manousiouthakis, 1989), including water pinch analysis (Wang and Smith, 1994) and hydrogen pinch analysis (Alves and Towler, 2002). Other process integration tools have also being developed for CO₂ emissions targeting (Linnhoff and Dhole, 1993), regional energy planning (Tan and Foo, 2007) and other areas. These methods have made major contributions towards a more energy efficient and sustainable process industry. But, how is it that such conceptual methods allow the confident generation of efficient process designs? As Kemp (2007) comments in his book *“to achieve optimality in most cases, particular insights are needed which are neither intuitively obvious nor provided by common sense”*. In other words, the power of process integration tools relies on the useful insights they provide which are difficult to unravel otherwise. For example, the energy targets in pinch analysis for heat exchanger networks provide information on the design goal and where and why a process is wasting energy. Another useful insight is the existence of a “pinch” temperature, which led to the name of the method and provides a starting point for design or retrofit.

Undoubtedly, process integration tools were essential elements that helped make crude oil refineries the efficient and flexible facilities they are today. This is the ultimate goal of the biorefinery concept for biomass processing. Although there is still a long way for biorefineries to reach such an advanced stage, the application of existing process integration tools and the generation of similar approaches addressing

the particularities of biorefineries will play a major role in their design. As shown in **Figure 1.2**, the research on biorefinery process integration must therefore be developed concurrently to technology development to advance faster in the learning curve towards efficient and sustainable designs.

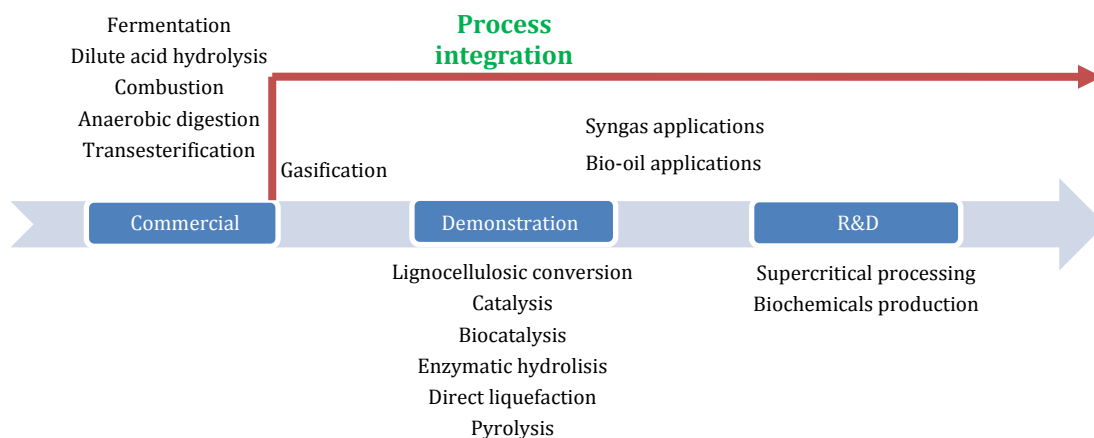


Figure 1.2 Processes technological convergence on the 2020 horizon showing the concurrent research on biorefinery process integration (Luguel, 2008).

Through process integration, biorefineries can be designed for high energy efficiency, maximum raw material utilisation and minimisation of emissions. High efficiency in energy and material utilisation allows saving resources while lower emissions contribute to preservation of the Earth's ecosystems, so that both resources and healthy environments can be made available for future generations, the ultimate goal of sustainable development. Therefore, the objective of the current work is to undertake fundamental research for the development and practical application of tools that will potentially contribute to the advancement of biorefineries towards their successful deployment as sustainable processing facilities.

1.3 Biorefinery design and integration

As in oil refineries, biorefinery designs must involve the fractionation of feedstocks into components that can undergo chemical, biochemical and/or thermochemical processes to produce versatile platforms which can be processed further, according to market demand, into biofuels and energy, added-value chemicals, polymers, food, etc. As crude oil is separated into light gases, naphtha, kerosene, gas oil, lubricants,

vacuum residue, asphalt and coke, biomass can be similarly first separated or converted into corresponding fractions such as biogas, syngas, sugars, hemicelluloses, cellulose, lignin, triglycerides, extractives and proteins. This creates the complexity required to implement process integration tools.

At the centre of the biorefinery design problem is the selection of the processes and their interconnections for the efficient conversion of biomass feedstocks into a set of multiple products. Due to the wide range of possibilities and their potential interactions, biorefinery design becomes a difficult task. Furthermore, the importance of environmental sustainability in the development of biorefineries suggests that this aspect must be considered early in the process design stage. The proper combinations of technologies, processing pathways and products derived from the understanding of the interactions between these elements is essential to establish systematic methods for biorefinery integration leading to sustainable process designs. **Figure 1.3** presents an overview of some of the possible combinations of feedstocks, processes, platforms and products that could provide enough complexity to generate scope for process integration.

It has been argued that biorefinery design can benefit from the application of existing and the development of new process integration tools for a better understanding of internal interactions and insightful analysis of economic and environmental performances. This research therefore exploits integration opportunities within biorefinery processes to address the sustainable biorefinery design challenge. The work takes advantage of process simulation in Aspen Plus®, spreadsheet calculations and life cycle analysis to model and analyse biorefinery systems and to demonstrate the new tools developed as part of the research. Various case studies are used throughout the thesis with a special focus on biorefineries mainly producing a biofuel, these being in a more advance stage of development and with greater availability of data.

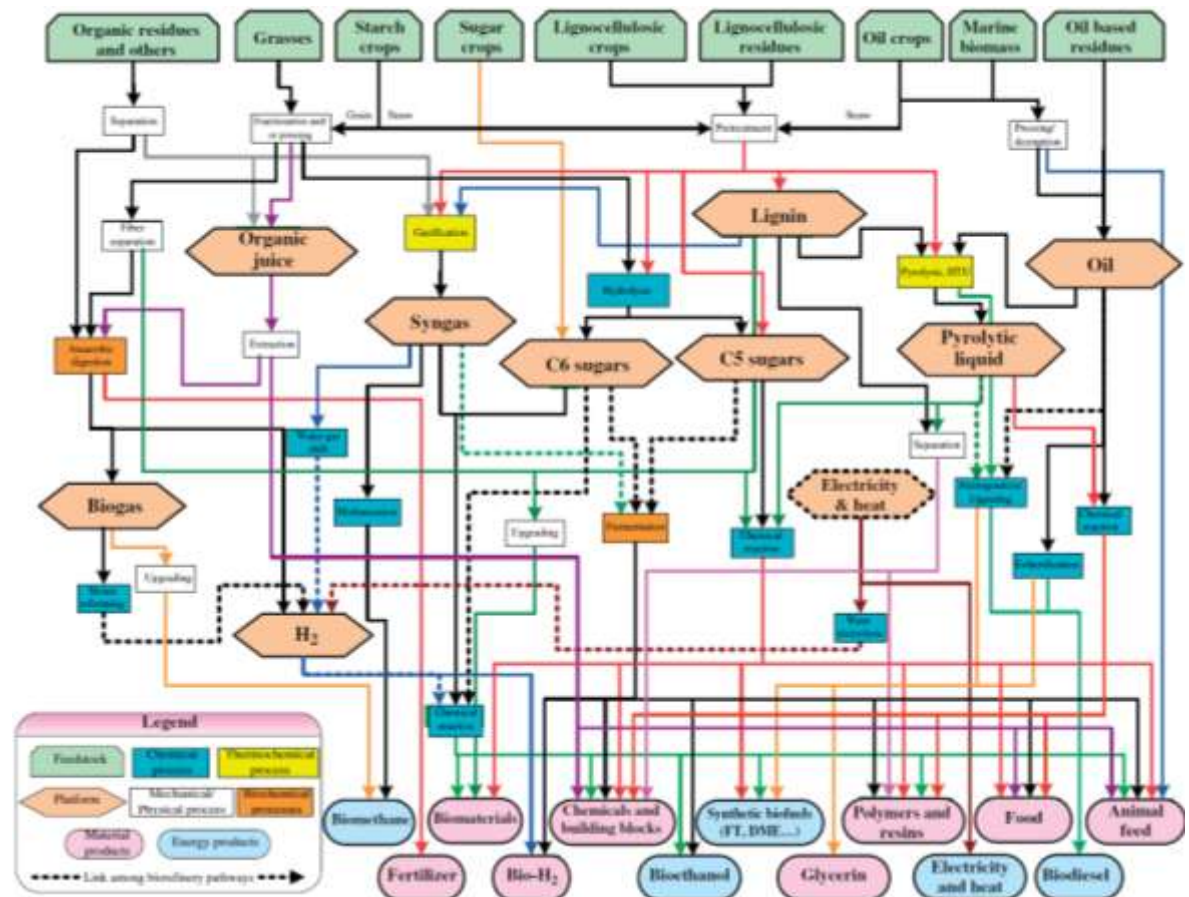


Figure 1.3 Overview of the different biorefinery features and their combinations forming alternative process configurations. *Source:* Cherubini et al. (2009).

1.4 Contribution of research

This research develops multilevel modelling approaches for holistic biorefinery system analysis comprising biomass cultivation, biorefinery process modelling, and economic and environmental impact assessment to identify and exploit energy and process-to-process material integration opportunities that lead to sustainable process designs. The main contributions resulting from this research are described as follows:

- 1) Production of fuel ethanol from biomass has been the fastest growing energy industry in recent years and is the major platform from which biorefineries are evolving. As well as being a major product, bioethanol can also be used as an in-process fluid, giving opportunities for integration. Following an approach based on mass pinch analysis, a method has been proposed for biorefinery integration wherein bioethanol is also utilised within the

processes for co-product generation. To avoid revenue losses due to the use of fresh amounts of a valuable product from one process in another biorefinery process, integration of streams containing the product is required for maximum recovery and utilisation efficiency. The process integration tool developed is called bioethanol pinch analysis and involves the construction of bioethanol composite curves and bioethanol surplus diagrams using spreadsheet calculations. The tool allows targeting minimum bioethanol utilisation as well as assessing network modifications. The effectiveness of the method has been demonstrated with a biorefinery producing bioethanol and arabinoxylan (AX) wherein bioethanol is required for AX extraction and streams with various purities are generated. It is envisaged that the approach can be extended to other cases where the biorefinery processes create opportunities for the exchange of product or co-product streams at different purity levels. This work is presented in **Chapter 2** in the form of a paper published in the *Journal of Applied Energy*.

- 2) Process integration tools such as heat pinch analysis and total site utility systems design are utilised in the current work to develop alternatives for biorefinery integration with the aim of reducing fossil energy use and GHG emissions of bioenergy production. This part of the research provides a framework for process modelling and simulation integrated with life cycle analysis for the assessment of alternatives in order to select the best integration alternative. While other studies provide assessment for gate-to-gate analysis, the life cycle approach utilised clearly shows the environmental impact sources and the hot spots in the overall system. The integration of models for biomass feedstock production is a key feature of the multilevel approach undertaken to track the effect of changes in the supply chain and cultivation practices.

The multilevel modelling approach was applied to wheat-based and *Jatropha* fruit-based biorefinery systems, showing evidence of the benefits of systematic process integration combined with careful environmental impact assessment. The research also shows how various platforms can be effectively coupled for process-to-process integration. This was demonstrated in a *Jatropha* biorefinery wherein the husk-derived syngas was utilised to

provide energy and raw materials to either biodiesel or green diesel process. In the biodiesel system syngas allowed the supply of methanol, while in the green diesel syngas provided hydrogen. The studies from this research are presented in **Chapter 3** for the wheat-based biorefinery in the form of a paper published in the *Journal of Biomass and Bioenergy* and in **Chapter 4** for the Jatropha-based biorefinery in the form of a paper submitted for publication in the *Journal of Biomass Conversion and Biorefinery*.

- 3) The previous contribution also showed that environmental impact assessment is not enough to select the best integrated process designs. Building upon the power of value analysis (Sadhukhan et al., 2003, 2008), a new methodology for the combined economic value and environmental impact analysis has been developed. Current environmental policy such as the EU Renewable energy directive for biofuels (European Union, 2009) is a new feature included in the multilevel approach described above. This contribution allows better visualisation of the impact and monetary flows in a process network through economic and environmental impact profiles and identification of hot spots. The representation of economic and environmental impact costs in a product profile provides insights that allow identification of integration pathways for environmental impact reduction and better distribution among the various products in order to achieve policy targets within a reasonable economic trade-off. Since the tool makes use of the multilevel modelling approach used in the contributions described above, it is sufficiently robust to capture variability in the properties, production system and market prices at the product side, and in market demands, prices and GHG saving policies at the product side. This work is presented in **Chapters 5** and **6** in the form of paper accepted for publication in the *Journal of Chemical Engineering Research and Design* and paper submitted for publication in the *Chemical Engineering Journal*.

As noted above, the thesis is presented as a series of papers that have been published or submitted to relevant journals. Each chapter contains a publication with a brief preamble discussing the research presented. The thesis ends with a **Conclusions** chapter that synthesises the work and its significance in the wider context of developments in integrated biorefineries.

Chapter 2

Bioethanol integration using mass pinch analysis

2.1 Preamble

As in petroleum refineries, biorefineries must follow the strategy of feedstock separation into more useful and treatable fractions, known as platforms or precursors. Then each fraction must create a production line to diversify their product portfolio and to increase profits and adaptability to the market conditions (Kamm et al., 2006; Demirbas, 2009; Cherubini et al., 2009; King, 2010). Biorefineries are currently relatively simple, mostly with one main product (e.g. bioethanol, biodiesel) and one or two co-products (e.g. DDGS and CO₂ in the case of bioethanol, oil extraction cake and glycerol in the case of biodiesel) and need to become more complex in order to create scope for improved energy and biomass conversion efficiencies. A combination of various high throughput technologies will allow converting the whole ton of biomass into value added products. These combinations will create a complex system able to exchange material (waste streams, platforms and products) and energy streams to supply their requirements and achieve self sufficiency (Sadhukha et al., 2008; Ng, 2010; Pham and El-Halwagi, 2012). The complexity gives the opportunity for process integration to increase energy efficiency, save water and reduce wastes and emissions. Thus, biorefinery design must be carried out adopting biorefinery integration strategies leading to improved economic and environmental sustainability.

Biorefineries could benefit from technologies well established in sugar and cereal processing such as the corn wet refineries (instead of waiting for, and relying solely on, a competitive and efficient lignocellulosic technology which is at its early stages of development). Major advances in generic biorefinery integration strategies could be achieved using existing infrastructure, with a view to transferring to the

lignocellulosic biorefineries once they become commercially available. Cereals (e.g. wheat, corn, rice) contain starch, the structure of which is between sugar and lignocellulose, and also feature lignocellulosic material in the form of bran. Both cereal and lignocellulosic biorefineries use a polymeric carbohydrate feedstock which generally involves solids in their process, their main differences relying on the pre-processing and transformations steps. With cereal biorefineries being closer to the lignocellulosic biorefineries, it is expected that any process integration development for the former could be of benefit for the latter.

The publication presented in this chapter exploits the increased complexity arising from a wheat-based biorefinery for the production of bioethanol, wheat and arabinoxylans (Sadhukhan et al., 2008). Arabinoxylans (AX) are the major dietary fibre component of wheat bran and a potential food additive for enhanced viscosity properties, gel formation, foam stabilisation and prebiotic activity (Courtin and Delcour, 2001, 2002; Maes and Delcour, 2001). In 2010, the total European food and beverage prebiotics market volume was 100 kt y⁻¹. By 2015, the market volume is estimated to be 205 kt y⁻¹ with an annual growth rate of 13.7 % (Frost and Sullivan, 2008). Being a natural polymer, it can find applications in the packaging films and composite industry. AX-based polymers could take part of the market share of bioplastics used in food packaging and in agricultural applications (e.g. cellulose, starch films, etc.) estimated to be 1100 kt y⁻¹ by 2016 (European Bioplastics, 2013). AX can be extracted using ethanol at 96% purity to wash the bran and at 70% purity to precipitate the AX product (Sadhukhan et al., 2008; Du et al., 2009; Misailidis et al., 2009). Various intermediate ethanol streams are produced in the process at purity levels ranging from 2.5% to 91.5%. This creates the scope for process integration of the AX production process for efficient and economical value added production within a biorefinery mainly producing bioethanol.

2.2 Discussion of publication 1

The paper presents the application of mass pinch analysis for integration of bioethanol streams in biorefineries producing and utilising ethanol within their processes. A systematic “bioethanol pinch” methodology adapted from the hydrogen pinch analysis is developed for the design and integration of bioethanol exchange

networks. As previously mentioned, the case study elaborated in the current paper is arabinoxylan extraction integrated with bioethanol production, in which ethanol streams of different purities are generated. The resulting exchange network featuring a set of bioethanol sources and demands is analysed to minimise fresh, high purity bioethanol product utilisation.

In the bioethanol pinch method, sources and demands are first arranged from low to high purities. Then, the bioethanol purity of the streams is plotted against their cumulative flow rates to form the bioethanol purity profile. This profile is made up of two composite curves, one for the sources and one for the demands and is divided in various flow rate intervals. The profiles are then used to identify where in the system bioethanol is being wasted and where the supply is constrained. When the source composite curve is below the demand composite curve, a deficit is found while an excess or surplus is found when the opposite occurs. From this analysis, simple algebraic calculations are carried out to determine the bioethanol surpluses and deficits for each flow rate interval at the various purity levels. The plot of surpluses and deficits against the purities generate a bioethanol surplus diagram. This diagram allows shifting the resulting curve until a pinch with the y-axis is found. The purity at which this happens is called the pinch purity and the flow rate difference between the initial and the shifted curves at this purity reveals the target for the minimum flow rate required by the bioethanol network. The pinch purity also divides the network in two regions and provides the starting point for process design. Furthermore, the pinch serves as a guideline for the placement of a purifier.

The graphical and analytical procedures described above allowed targeting for minimum fresh bioethanol consumption in the AX production process. The method also proved useful for evaluation of a purifier for bioethanol recovery. The final bioethanol network design uses 94% less bioethanol product than the non-integrated network thus avoiding significant revenue losses.

Overall, this research paper highlights that within a biorefinery there may be product streams that are also potentially working fluids (e.g. solvents and precipitants as in the case of ethanol, chemical raw materials and fuels for utility generation) and how the resulting complexity can be used to generate integrated biorefinery designs. This particular application of pinch analysis is demonstrated for the first time in this

paper. The approach could be adopted by any other comparable product-based biorefineries wherein material streams may be both final products and in-process streams.

Methodological aspects

Although the bioethanol pinch method is explained within the paper, some aspects of regarding data for the case study and the tools used for some calculations are clarified in this section.

The initial mass balance of the bioethanol network under study has been taken from the paper by Sadhukhan et al. (2008). In the process described there, 99.6% purity is produced. Since the AX extraction step requires ethanol at 96% (Du et al., 2009; Misailidis et al., 2009), the stream is diluted with water (or with diluted streams available if the process is not affected by impurities). As mentioned in the publication presented in this chapter, the use of external bioethanol utility of high purity provides ethanol surpluses that can be easily exchanged to balance deficits at lower purities. Alternatively, ethanol could be directly supplied at 96% purity from the rectifier column (which produces bioethanol at 96% purity) of the purification section in the bioethanol production process.

The mass balances required in the bioethanol network design step, after finding the bioethanol pinch, consist of a system of linear equations that are solved by the method of repeated elimination of variables or solved simultaneously by using well known methods (e.g. Gaussian elimination). Since the process studied is not complex and the system of equations was not large, the calculations were carried out in a spreadsheet. Once the minimum fresh bioethanol target is known, the mass balances are solved first for the units above the pinch. Since the pinch is based on the overall mass balance of the network (equation 1 of the paper), the bioethanol available above the pinch is equal or higher than the bioethanol required by the demands. Thus, for every demand process unit, the mass balance equations to be satisfied are:

a) Mass balance on the total flow required by a bioethanol demand:

$$F_{D,j} = \sum_{i=1}^{nss} F_{S,i,j} \quad \text{A)}$$

where $F_{D,j}$ is the total stream flow rate required by demand j

$F_{S,i,j}$ is the flow rate of the stream from source i to demand j

nss is the number of supply or source streams

b) Mass balance on ethanol:

$$F_{D,j} x_{D,j} = \sum_{i=1}^{nss} F_{S,i,j} x_{D,i} \quad \text{B)}$$

where $x_{D,j}$ is the bioethanol purity or concentration required for the process carried out by demand j

$x_{D,i}$ is the bioethanol purity or concentration of the stream from source i

c) Since the total flow from a source can be split to supply more than one demand, the following constraint must be also observed for a source i :

$$F_{S,i} \geq \sum_{j=1}^{nss} F_{S,i,j} \quad \text{C)}$$

Any excess of bioethanol source streams from the design above the pinch is used for the design below the pinch. This does not violate the rule stating that bioethanol must not be exchanged across the pinch. Such rule only applies when a source from below the pinch is used to supply a demand above the pinch, as explained in the publication presented in this chapter. The solved mass balance for the design above the pinch in the first pinched system (before incorporation of a purifier) is shown in Figure 6 of the publication. The pinch analysis method also ensures that the bioethanol available below the pinch is equal or higher than the bioethanol required by the demands. Thus, after solving the mass balance above the pinch, the mass balance below the pinch can be solved in a similar manner (i.e. using equations A and B given above subject to the constraint in equation C). The solved mass balance above and below the pinch for the final network design is shown in Figure 7 of the publication. For systems with more than four equations, hand

calculations in spreadsheet might be complicated and the use of the *Solver* feature in Microsoft Excel[®] is more convenient.

It might be argued that the use of bioethanol in another process instead of being sold as fuel will generate losses. However, as the same study by Sadhukhan et al. (2008) shows, the economic value of the AX (2000 £ t^{-1}) could be more than 3 times the value of bioethanol (590 £ t^{-1}). Furthermore, the bioethanol pinch was conceived with the aim to minimise bioethanol losses in AX production. The total production of bioethanol at 99.6% purity from fermentation is 114.5 kt y^{-1} and the integrated AX process network, after application of the integration method, uses about 2.5 kt y^{-1} of bioethanol. This gives a net bioethanol production for sale of 112 kt y^{-1} . Thus, the bioethanol loss is of just 2%. For the product prices in Sadhukhan et al. (2008), as given above, the bioethanol revenue loss is 1.45 M£ y^{-1} while the revenue from the sale of the 2460 t y^{-1} of AX co-produced is 4.92 M£ y^{-1} (thus the revenue from AX is about 240% higher than the bioethanol revenue loss). Thus, the use of bioethanol for the AX process is economically justified. The economic margin considering costs of production is presented in the publication in Chapter 5, where the trade-off between economic potential and environmental impact is also discussed.

For the purposes of a preliminary economic analysis, only the bare module capital cost is considered. Other associated costs such as contingency and maintenance are not considered. However, for preliminary estimation, these costs are generally factored from the bare module capital costs by a certain percentage (e.g. 10%; Peters et al., 2003; Turton et al., 2009). Therefore, the base values of the capital costs of any of the options evaluated in the publication will be scaled by the same factor and the conclusions will not be affected. The main factor affecting capital costs is capacity, and this factor is considered in the estimation of the bare module capital cost (Turton et al., 2009). The capital cost was annualised using a factor of 28%, which was estimated for the whole biorefinery under study by Sadhukhan et al. using internal rate of return of 12%, 39 months of construction period and net present value and cash flow calculations (details in Sadhukhan et al., 2008).

Publication 1: Martinez-Hernandez, E., Sadhukhan, J., Campbell, G.M., 2013. *Integration of bioethanol as an in-process material in biorefineries using mass pinch analysis.* Applied Energy 104, 517–526.



Integration of bioethanol as an in-process material in biorefineries using mass pinch analysis

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HIGHLIGHTS

- Bioethanol integration approach based on mass pinch analysis.
- Bioethanol exchange network design to maximise recovery between sources and demands.
- Graphical targeting approach allows minimum fresh bioethanol consumption.
- Biorefinery debottlenecking by bioethanol integration and added value co-production.
- Graphical targeting and cost-benefit analyses for synthesis and retrofit design.

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ABSTRACT

A biorefinery involving internal stream reuse and recycling (including products and co-products) should result in better biomass resource utilisation, leading to a system with increased efficiency, flexibility, profitability and sustainability. To benefit from those advantages, process integration methodologies need to be applied to understand, analyse and design highly integrated biorefineries. A bioethanol integration approach based on mass pinch analysis is presented in this work for the analysis and design of product exchange networks formed in biorefinery pathways featuring a set of processing units (sources and demands) producing or utilising bioethanol. The method is useful to identify system debottleneck opportunities and alternatives for bioethanol network integration that improve utilisation efficiency in biorefineries with added value co-products. This is demonstrated by a case study using a biorefinery producing bioethanol from wheat with arabinosyl (AX) co-production using bioethanol for AX precipitation. The final integrated bioethanol network design allowed the reduction of bioethanol product utilisation by 94%, avoiding significant revenue losses.

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1. Introduction

Starch crops (e.g. corn, wheat), sugar crops (sugar cane and sugar beet) and lignocellulosic material (agricultural residues, wood, grass, etc.) are the main biomass feedstocks employed for bioethanol production [1–4]. Even in the case of processes using biomass feedstocks, such as algae [5,6] and black liquor [7] to produce other biofuels such as biodiesel or methanol, some valuable components in these feedstocks represent a significant fraction that ends up in low value by-products. In the case of starch crops, the by-product is the Distillers Dried Grains with Solubles (DDGS). As supply of bioethanol increases, more DDGS is produced resulting in a lower market value. Extraction of valuable biomass feedstock fractions

in added value products along with process integration is then necessary to enhance the economics of biorefinery systems producing bioethanol [8–10]. In addition to its intended application as a product to be used as transportation fuel, ethanol could also become an important intermediate feedstock or utility that could be used within a biorefinery. For example, ethanol can be used as a solvent for fractionation or extraction of added value products from biomass [8]. This offers potential for effective integration of various processing pathways to achieve efficient use of bioethanol within a biorefinery, especially where there are various source streams containing bioethanol at different concentrations and various demands requiring bioethanol.

Methodologies for biorefinery process design have emerged to address the particular nature of biomass processing and the complexity of the task of biorefinery integration at different levels. Feedstocks, processing technologies and products are the three

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levels of complexity concerning the integration of biorefineries [11]. There are methodologies based on process integration and assessment tools to improve internal material and energy recovery within a site and reduce external resource requirements. In the case of bioethanol production, heat pinch analysis, water pinch analysis and life cycle assessment have been applied to several configurations including value added production pathways and combined heat and power generation [11–23]. In addition, there are methodologies that combine process synthesis and optimisation through mathematical programming allowing screening of alternatives and creation of innovative biorefinery configurations [24–27]. Pham and El-Halwagi have proposed a “forward-backward” approach for biorefinery process synthesis and optimisation when a feedstock and a target product are specified using matching and interception procedures [25]. The method was applied for bio-alcohols production from lignocellulosic feedstocks and provided a configuration with optimised pathways between feedstock and end products along with possible open pathways for by-product production. However, the pre-treatment of biomass is not included as a conversion step and the biorefinery integration at the product level (i.e. potential utilisation of the various products within the biorefinery processes) is not considered. The interactions resulting from product integration could potentially reduce import of raw materials.

Whilst optimisation frameworks are worthwhile when well established technologies and real plant data are available, their solutions can be computationally demanding as more advanced and complex process technologies will emerge. Methods giving knowledge about the behaviour of integrated biorefinery processing networks, by intervention of the process engineers throughout the design task, can be of great value at the current stage of the learning curve of the field of biorefineries. The knowledge acquired then can be introduced within the mathematical formulations for better representation of a process and improved optimisation results. Furthermore, the potential for mass integration of biorefinery products within the processes has not been explored in the mentioned methodologies. In this sense, conceptual developments using the pinch analysis approach based on source–demand models of process integration can prove to be valuable as in the case of energy sector planning [28,29].

As discussed above, although the traditional process integration tools have been successfully applied for reduction of energy and environmental impact and to maximise profits, new tools are required to enable integrated processing of starch and lignocellulosic feedstocks for bioethanol production, in which ethanol can be used as utility for biomass fractionation or pretreatment as well as chemical reactant. A systematic “bioethanol pinch” methodology for the design and analysis of bioethanol exchange networks is proposed in this paper, adapted from hydrogen pinch analysis [30]. The methodology is a particular case of mass pinch analysis for synthesis of mass exchange networks [31]. According to the extended definition recently introduced by Ponce-Ortega et al. [32], it is an example of process intensification which includes any activity that reduces the use of material utilities and/or feedstock. The case study elaborated in the current paper is arabinoxylan (AX) extraction integrated with bioethanol production, in which ethanol streams of different purities are required for arabinoxylan precipitation and for feedstock washing [8,33,34]. The proposed methodology has been used to minimise the bioethanol requirement within the biorefinery.

In Fig. 1, opportunities for bioethanol integration between sources and demands (streams numbered 1–12) within a biorefinery producing bioethanol and arabinoxylans from wheat have been identified. The route to extract arabinoxylans (AX) using bioethanol to precipitate the extracted AX presented in this figure has recently been explored [8,33,34]. In this process ethanol is used for

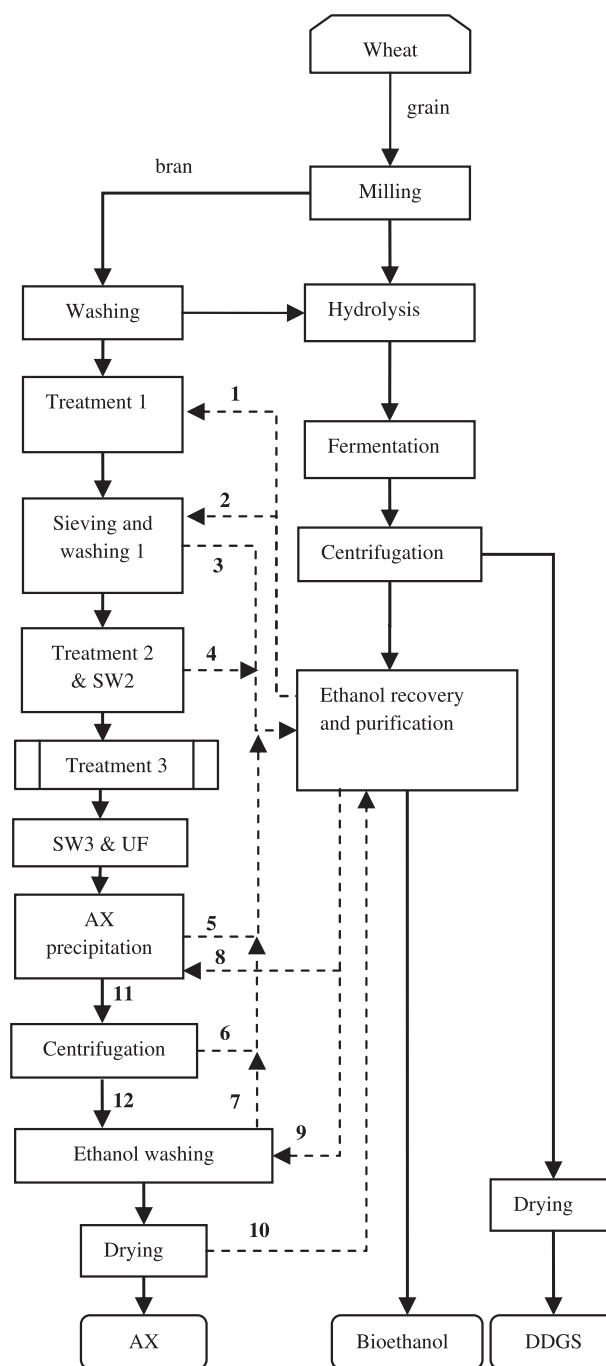


Fig. 1. Bioethanol pathways in a biorefinery using starch and lignocellulosic feedstock. The various bioethanol rich streams are indicated by the dashed lines. SW: Sieving and washing, UF: ultrafiltration, AX: arabinoxylan, DDGS: distillers dried grains with solubles.

bran purification (at 70% purity) and for AX precipitation and washing (at 96% purity). In a more complex design, the Organosolv process could be used to fractionate lignocellulosic materials for the production of bioethanol and other added value products. The Organosolv process similarly uses ethanol within the process at 50–60% purity to separate lignocellulosic feedstock into cellulose, hemicellulose and lignin [35]. The cellulose and hemicellulose fractions are sent to hydrolysis to produce more bioethanol whilst the lignin fraction is refined for further valorisation (in composites, wood-adhesives, fuel additives, etc.) or as fuel. Some furfural is also produced which can be sold as a solvent. A third common process

pathway of bioethanol is its conversion into ethylene and subsequent polymerization into polyethylene [36].

A preliminary set of demands and sources for the targeted product interacting in the form of a *product exchange network* (PEN) can be constructed and analysed following the approach from pinch analysis [37], water pinch analysis [38–40], hydrogen pinch analysis [30,41], CO₂ emissions targeting [28] and mass pinch analysis [24,31]. The sub-network generated would contain all the integration alternatives between product sources and product demands also in relation to co-products from a biorefinery. The sources and demands would produce intermediate streams containing the targeted product at different purities. The PEN can be expanded to include all intermediate unit operations and streams with more detailed process data and constraints. New routes for biomass processing can be synthesised with emphasis on efficient use of feedstocks, waste minimisation and polygeneration flexibility. Even more, alternative or complementary feedstocks can be also identified. If the PEN operates at or near the minimum supply and within the constraints set by the requirements of the product demands (both in quality and quantity), then the system is expected to operate in the most efficient manner. However, without a targeting method for the minimum bioethanol supply, it is difficult to know how well the network is performing. A systematic approach for targeting for minimum fresh marketable product requirement in a PEN within a biorefinery is presented in this paper, taking the particular case of bioethanol. Fig. 1 illustrates a complex biorefinery with integrated AX extraction in which ethanol features as a process stream of varying purity as well as a product of the biorefinery.

2. Methodology

2.1. Constraints for bioethanol pinch analysis

The bioethanol pinch analysis tool is intended to establish the minimum flow rate of bioethanol that can be used as a target for an integrated biorefinery design. In principle, this target can be decided assuming that any source can supply any demand. However, the minimum fresh bioethanol supply required by a system is driven by the constraints imposed by the processes involved and material conservation principles. Those constraints include the pressure, temperature, amount and nature of impurities, flow rate, purity, etc. Furthermore, the constraints may specifically include: minimum flow rate and/or purity of supply to a demand (e.g. 70% bioethanol for bran purification), limiting bioethanol content for process unit operations (e.g. a bioethanol concentration of 65% required for AX precipitation), limiting impurity content, etc. The nature of the feedstock and the composition of the intermediate streams as well as the purpose of the product are also important. Since the chemical species involved in various bioethanol pathways may not be the same, the bioethanol-containing streams in Fig. 1 are not all necessarily exchangeable. For example, the AX pathway involves components like protein, sugars and glucans, and the final product must meet certain composition specification in order to be used as food additive or other potential application. Thus, an ethanol recovery unit in the AX process might be required. The purity and flow rate constraints imposed by the bioethanol demand streams are captured by formulating a material balance on the total streams and a material balance on bioethanol. This formulation constitutes the main underlying principle for the bioethanol integration technique presented here.

From conservation principles, the total amount of ethanol available from the sources must be in excess or equal to the total amount of ethanol required by the demands as a first necessary condition for the network to be feasible. The condition for material

balance of the whole bioethanol network can be expressed in the following equation:

$$\sum_{i=1}^{ns} F_{S,i} = \sum_{j=1}^{nD} F_{D,j} + \sum_{k=1}^{nW} F_{W,k} \quad (1)$$

where $F_{S,i}$ is the flow rate available from source i ; $F_{D,j}$ is the flow rate required by demand j ; $F_{W,k}$ is the flow rate of waste stream k sent to treatment (e.g. ethanol recovery or wastewater treatment); and n_s , n_D and n_W are the numbers of sources, demands and waste streams, respectively, in the network.

2.2. Bioethanol composite curves

After the selection of appropriate bioethanol sources and demands, the source and demand streams are combined into the source composite curve (SCC) and the demand composite curve (DCC), respectively, on purity against flow rate plots, following the construction of composite curves for mass exchanger network designs [30,31,38–41]. The composite curve represents the total amount of mass flow rate to be removed in each purity interval. Fig. 2a shows a generic diagram with the SCC and DCC comprising three source streams and three demand streams. To construct the SCC, the source streams are plotted in the order of decreasing purity and cumulative flow rates forming a cascade of horizontal steps. Each step in the SCC indicates the total flow rate of bioethanol streams available at the corresponding purity level. The DCC is constructed following the same procedure. Each step in the DCC indicates the total flow rate of bioethanol streams required at the corresponding purity level. According to the bioethanol conservation principle, a SCC shorter than the DCC would indicate that the material balance on the total stream is violated for at least one of the demand streams. If the area covered by the SCC is larger than that of the DCC, then there is excess bioethanol in the system. When the excess bioethanol comes from a source stream that is not exchangeable or has low ethanol content, some amount of bioethanol would be lost into wastewater treatment (WWT).

The areas enclosed between the SCC and DCC represent the bioethanol pockets in the system, indicated in Fig. 2a. If the SCC is above the DCC for a given range of bioethanol purity, then the sources provide more bioethanol than is required by the demands at that particular purity range. Here, a bioethanol excess or surplus (+) appears. This surplus can be made available to compensate for a deficit in bioethanol supply at a lower purity. If the SCC is below the DCC, the bioethanol from the sources is not enough to cover the demands producing a deficit (–) of bioethanol. This means that the demands require bioethanol at purity higher than the purity of the corresponding sources. This deficit can be compensated only by the surplus bioethanol of a higher purity which can be mixed with the lower purity sources to raise the bioethanol content until the purity constraint of the demand is met. The balance of bioethanol pockets (surplus and deficits) at the various purity levels is the key for systems integration and debottlenecking.

2.3. Bioethanol surplus diagram

In addition to the amount required, bioethanol must also be supplied at appropriate purities required by the demand streams. Thus, the bioethanol excess/deficit must be identified at various purity levels from the composite curves. The bioethanol excess or deficit can be determined for each flow interval of the combined SCC and DCC. The diagram in Fig. 2a is divided into six flow intervals (I–VI). The number of intervals in the system is equal to the total number of flow rate segments. The area between the SCC and DCC in a particular interval i represents the material balance

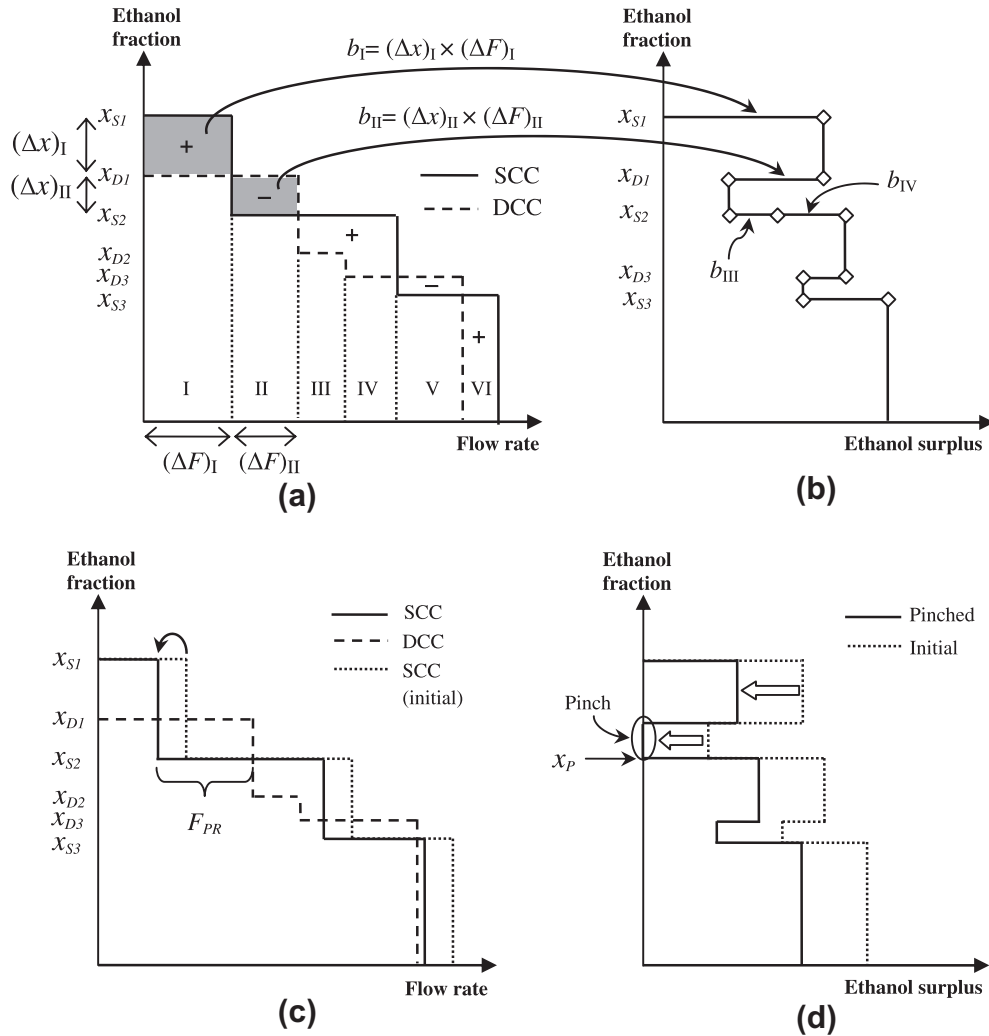


Fig. 2. (a) Source composite curve (SCC) and demand composite curve (DCC) showing how the areas in the pockets are related to the horizontal segments in the corresponding, (b) bioethanol surplus diagram. The bioethanol surplus is calculated for each of the flow rate intervals (I–VI). (c) The reduction in utility flow rate displaces the SCC towards the left producing a and (d) shift in the surplus diagram until pinched with the y-axis.

and it is equal to the bioethanol flow rate b_i , as shown in the following equation:

$$b_i = (x_{Si} - x_{Di}) \times (F_{Ui} - F_{Li}) \quad (2)$$

where x_{Si} and x_{Di} are the purities of the source and demand in the interval, respectively; F_{Ui} and F_{Li} are the upper and lower bounds of the flow interval, respectively. The net cumulative surplus (or deficit) bioethanol at each given flow rate, when plotted in purity vs. flow rate, forms the *bioethanol surplus diagram*. The bioethanol surplus diagram generated from the bioethanol composite curves in Fig. 2a is presented in Fig. 2b, showing the pocket areas represented as horizontal segments. In this representation, the maximum value between x_S and x_D is taken for the y-axis, in order to set a common scale.

The *bioethanol surplus diagram* displays the net flow rate characteristics of a network versus the purity of bioethanol. The significance of the surplus diagram is that it indicates if the flow rates of bioethanol utilities can be reduced, lowering the fresh bioethanol requirement, within given constraints. If the surplus is negative at any flow interval between F_{Ui} and F_{Li} (i.e. surplus curve crosses y-axis), then the system is not receiving the required amount of ethanol at the adequate purity. In that case, at least one of the constraints on bioethanol flow rate imposed by the demands cannot be satisfied by the sources, rendering the system unfeasible. This

situation would lead to using additional amounts of fresh ethanol or higher-purity ethanol. Therefore, the second necessary condition for system feasibility is that the material balance on ethanol in the overall system (i.e. the cumulative ethanol flow rate) must always be positive. This means that if the entire bioethanol surplus curve lies at or above zero bioethanol flow rate, then the second condition for a feasible system is achieved. If both the first (Eq. (1)) and second necessary conditions are met, then the bioethanol integration problem has at least one feasible solution.

One of the possible solutions is when the bioethanol network is constrained on bioethanol supply. In this case the bioethanol requirements are just met so that any reduction in the supply creates a negative surplus making the network unfeasible. A bioethanol network featuring such a constraint would present at least one place in the bioethanol surplus diagram where the bioethanol surplus is equal to zero. At this point, a pinch can be appreciated where the bioethanol surplus curve touches, but does not cross, the y-axis. This “bioethanol pinch” sets the minimum bioethanol consumption in the network.

2.4. Bioethanol pinch and targeting

The bioethanol pinch corresponds to the point at which the bioethanol network has neither excess nor deficit. As in other process

integration techniques, identification of the pinch point helps establishing the minimum bioethanol utility targets, corresponding to the maximum bioethanol reuse in view of an integrated and efficient biorefinery flowsheet design. If a network has excess ethanol sources even after maximum reuse indicated by the bioethanol pinch point, opportunities for system improvement or debottlenecking can be further explored by adding bioethanol production or purification units or by fresh ethanol imports.

Fig. 2c illustrates how the flow rate of the first source is varied until a pinch occurs in the bioethanol surplus diagram (Fig. 2d). The purity of the bioethanol source at the pinch corresponds to the bioethanol pinch purity (x_p). The bioethanol pinch appears in the surplus diagram by a discontinuity segment at surplus equal to zero between x_p and the corresponding x_D . In the pinched diagram (Fig. 2d), the surplus curve is shifted towards the y-axis showing a reduction in the bioethanol utility requirement. Similar to the hydrogen pinch, the bioethanol pinch divides the overall bioethanol network into a subsystem with net zero ethanol surplus (region above the pinch) and a subsystem with net positive ethanol surplus (region below the pinch). Above the pinch, there is a portion of the flow rate from the source stream at the pinch purity indicated as F_{PR} (Fig. 2c). This flow rate corresponds to the amount that must be reused by the demand streams above the pinch to meet the bioethanol supply target. In intervals where a net flow rate surplus exists, the net flow rate can be cascaded to lower purity intervals. Once the demand for bioethanol at lower purity intervals is entirely satisfied, any other excess bioethanol available can be sold to the market. In intervals where a net deficit of bioethanol flow rate exists, the excess bioethanol from higher purity intervals must be used first. Only after exhausting flow rate surpluses from higher purity intervals, external bioethanol utilities can be applied. Other implications from the bioethanol pinch for the integration of a bioethanol exchange network are discussed below.

As mentioned before, the network is divided into a region above and below the pinch as shown in the pinched surplus diagram (continuous line in Fig. 2d). Since the subsystem above the pinch is balanced, reusing a bioethanol stream from below the pinch implies the transference of the same amount from a source above the pinch (at higher purity) across the pinch to preserve the material balance. This produces a reduction in ethanol surplus above the pinch, and additional utility must be supplied as a penalty to keep the system balanced. Finally, the requirement of fresh ethanol would exceed the minimum target identified by the bioethanol pinch method. Thus, the bioethanol streams must never be directly exchanged across the pinch. As with pinch analysis in other contexts, this is the first fundamental principle for the design of a bioethanol exchange network at minimum supply.

A second bioethanol integration principle is deduced for the purifier placement from the implications of the pinch point. A purifier placed below the pinch purity would make purer ethanol in a region of surplus that will end up as waste stream since it cannot be exchanged to supply a demand above the pinch. Thus, a purifier should always be placed across the pinch purity in order to exchange ethanol from a region of surplus to a region of limited supply. This can lead to a further minimization of the fresh bioethanol utility. The application of the bioethanol pinch targeting method to minimise the fresh bioethanol utility supply and the use of the integration principles for the design of a bioethanol exchange network are demonstrated in the following section using a case study. The general strategy for network analysis, design and integration is depicted in Fig. 3.

2.5. Case study

For an effective demonstration of the bioethanol integration method, the processing pathways co-producing AX in Fig. 1 were

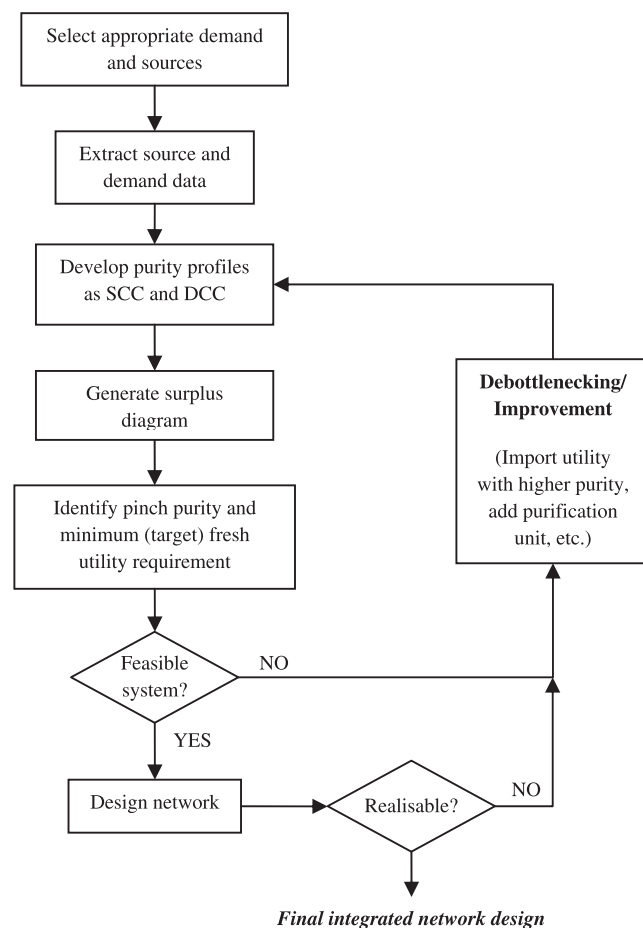


Fig. 3. General strategy for bioethanol integration.

analysed. The initial PEN showing the bioethanol demands and sources is depicted in Fig. 4. The bases are: a biorefinery processing capacity of 340,000 t/y of wheat from which 13,600 t/y of bran is separated to produce 2460 t/y of 70% purity AX [8].

2.5.1. Demands and sources

The main source is the fresh bioethanol produced at 99.6% purity, which is diluted to supply 96% ethanol to the precipitation unit (PPU-1) and washing unit 2 (WSU-2). The AX precipitation requires enough ethanol for a final concentration of about 65%. The waste streams rich in bioethanol resulting from PPU-1, WSU-2 and centrifugation (CFG-2) are recycled and supplemented with a fresh bioethanol top-up stream. Those streams are mixed to supply the 70% ethanol required by the treatment unit 1 (TMU-1) and sieving and washing unit 1 (SWU-1). The stream resulting from SWU-1 contains the ethanol extractable components from the bran which are not desirable for the AX product. Therefore, this stream cannot be directly exchanged in the system. The sieving and washing unit 2 (SWU-2) produces a waste stream with high flow rate but poor ethanol content. Streams from SWU-1 and SWU-2 can be sent to the recovery section or wastewater treatment (WWT). The vapour stream from the rotary dryer (RDY-2) is lost as waste but, if it is condensed, an exchangeable bioethanol rich stream could be generated. Source and demand streams in the order of decreasing purity are presented in Table 1 for the data extracted from the example bioethanol network in Fig. 4.

2.5.2. Finding the bioethanol pinch and target

The SCC (initial) and DCC generated for the data in Table 1 are presented in Fig. 5a. Two pockets of high amounts of ethanol in

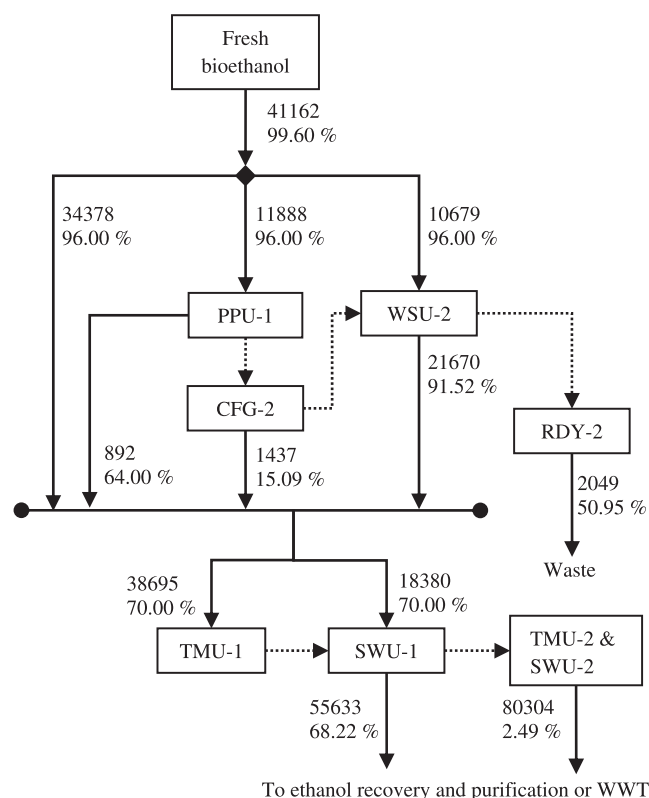


Fig. 4. Bioethanol network in the production process of arabinosyran (70% purity) from wheat bran. The balance in the first diamond knot is water required for bioethanol dilution from 99.6% purity to 96% purity. WWT: wastewater treatment. Flow rates in t/y.

excess and one small pocket of ethanol in deficit can be observed. This indicates that the system may not be using the bioethanol available in an efficient manner. To determine how well the system is performing in terms of efficient reuse of bioethanol, the bioethanol targeting approach discussed in Section 2.4 is applied. In order to find the bioethanol supply target, the surplus curve must firstly be pinched by varying the flow rate of bioethanol supplied to the network. Not all the sources can accept the flow rate to be changed or reduced since these flow rates may be required for the normal operation of the processes. The bioethanol sources that are flexible with respect to flow rate are thus the utility imports to the network from external suppliers or other processes within the biorefinery.

Table 1
Bioethanol demand and source data extracted from the example bioethanol network.

ID	Process unit	Stream in Fig. 1	Flow rate (t/y)	Ethanol mass fraction	Cumulative flow (t/y)
Demands					
D1	PPU-1	8	11,888	0.9600	11,888
D2	WSU-2	9	10,679	0.9600	22,567
D3	TMU-1	1	38,695	0.7000	61,262
D4	SWU-1	2	18,380	0.7000	79,642
Sources					
S1	Fresh bioethanol		41,162	0.9960	41,162
S2	WSU-2	7	21,670	0.9152	62,832
S3	SWU-1	3	55,633	0.6822	1,18,465
S4	PPU-1	5	892	0.6400	1,19,357
S6	RDY-2	10	2049	0.5095	1,21,406
S7	CFG-2	6	1437	0.1509	1,22,843
S8	SWU-2	4	80,304	0.0249	2,03,147

In case of AX co-production the interest is to reduce the amount of fresh bioethanol product to be used, thus the flow rate of this utility can be varied. This corresponds to the bioethanol stream with the highest purity which would also have the highest cost. The targeting procedure thus can be applied to reduce the bioethanol utility supply with the highest flow rate and/or with the highest cost or purity.

The fresh bioethanol supply (at 99.6% purity) was reduced (Fig. 5a) until a bioethanol pinch occurred at a purity of 91.52% (Fig. 5b) for a flow rate of 12,512 t/y. This corresponds to the target for the minimum ethanol import for a feasible exchange network. The length of the displacement of the first step in the SCC indicates the amount of fresh bioethanol product (at 99.6% purity) that can be saved. Thus, the amount of ethanol utility import can be reduced by 28,650 t/y from the initial 41,162 t/y (Table 1). This means almost 70% less bioethanol product would be spent in AX co-production. Since the integrated design needs to be economically viable, the bioethanol network integration options need to achieve an increase in profitability. The analysis may require several iterations and a spreadsheet tool would avoid the tedious calculation and graphical construction. Thus, the bioethanol pinch method has been adapted to a user friendly software tool using Excel-VBA that can be made available upon request.

2.5.3. Bioethanol network design and integration

Fig. 5b reveals that the ethanol supplied to the initial bioethanol network is not being used efficiently. The arrows showing the displacement between the original and the pinched diagram indicate that there are substantial amounts of ethanol that can be saved for other purposes. This sets the scope for improvement of the network design following the bioethanol integration strategy in Fig. 3. The pinch point indicates that all units producing and requiring ethanol at purity equal or higher than x_p must be exchanged above the pinch. Then, simultaneous mass balances must be solved to determine the flow rates exchanged between them.

Fig. 6 shows the resulting bioethanol exchange network above the pinch. Notice that some of the bioethanol from WSU-2 is sent below the pinch, but not across the pinch since the stream is at the pinch purity $x_p = 91.52\%$. Thus, the first criterion for bioethanol exchange network design is satisfied. This in turn also shows that the initial network was violating this criterion by using great amounts of fresh bioethanol (at 99.6%) from above the pinch to supply a demand (at 70%) below the pinch, crossing x_p . Notice how the recycle flow rate F_{PR} (Fig. 5a) from WSU-2 is used efficiently. Although Fig. 5a indicates that the remaining stream from WSU-2 at 91.52% can be mixed with the stream from SWU-1 at 68.22% to supply ethanol for TMU-1 and SWU-1 at 70%, due to the impurity content (ethanol extractable components) of the stream from SWU-1, this option cannot be considered. In this case, other debottlenecking options must be explored to improve the network design and performance. One of the options is to import a utility with higher purity in order to increase the exchangeable surplus. However, in the example network the ethanol is supplied at the highest possible purity, which corresponds to the pure bioethanol product. Another option is to purify a stream in order to make more ethanol available to the system at a higher purity. The integration of a purification unit is thus evaluated in this case study by using the bioethanol pinch analysis method.

Although the bioethanol pinch does not indicate which stream to purify, the technique is useful to determine whether the integration of a purification unit to the system has a potential for additional savings. The first stream of interest is the waste from SWU-1. This stream has a high flow rate (55,633 t/y) at medium level purity of 68.22% (Table 1), but the stream contains impurities not desirable in the downstream processing. Since most of the impurities are solids, they can be easily separated. Although the

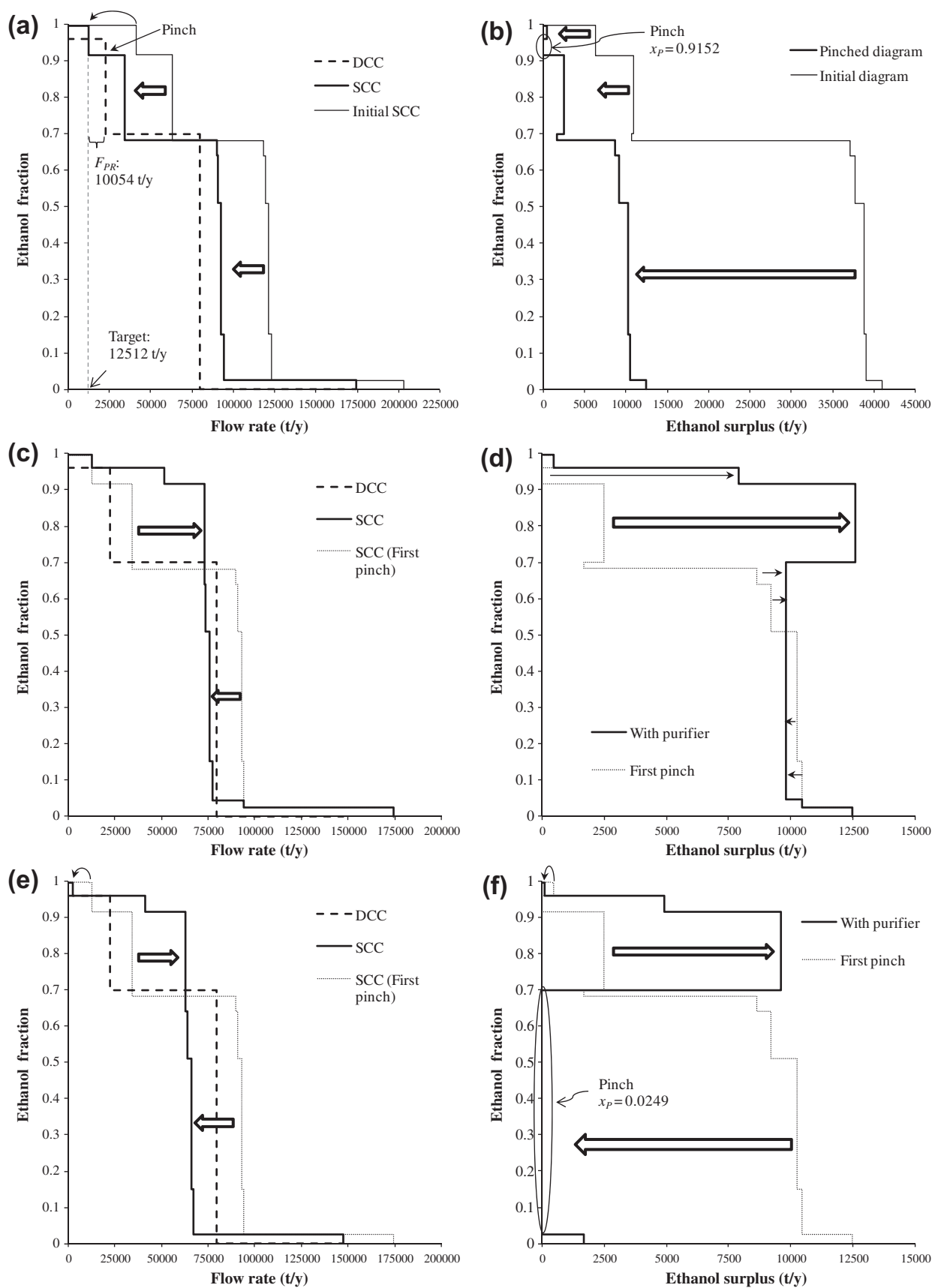


Fig. 5. Evolution of the bioethanol composite curves and surplus diagram throughout the bioethanol integration process. (a) The initial and pinched bioethanol composite curves and the corresponding, (b) bioethanol surplus diagrams for the example network. (c) The composite curves and (d) bioethanol surplus diagrams before and after integrating a purification unit to the system. (e) The pinched ethanol composite curves and (f) surplus diagram with and without purifier.

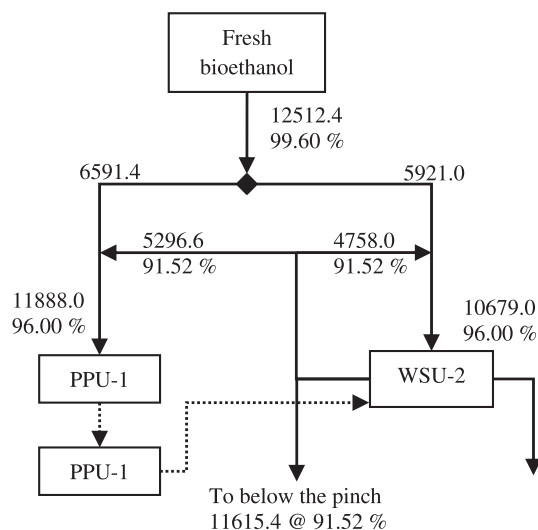


Fig. 6. The bioethanol exchange network design above the pinch for the target fresh bioethanol makeup. Flow rates in t/y.

ethanol content is appropriate for the rectifier column from the purification section of the biorefinery, adding a stream with high solids content (more than 20%) could not be desirable for the operation of the column since at this stage almost all the solids from fermentation have been removed. Furthermore, the installation of an additional unit would provide operational flexibility for ethanol purification. Assuming 98% ethanol recovery, the new purification unit produces 38,745 t/y at 96% purity and 16,888 t/y of a solids-containing stream with an ethanol content of 4.49%. The bottom stream of the purifier is not exchangeable because it contains the impurities removed. Thus, this source stream is excluded from further analysis. The purity profiles and the surplus diagram, after the introduction of a purifier in the network and before finding the pinch, are depicted in Fig. 5c and d, respectively. The new step in the SCC represents the new stream source in the system.

Fig. 5c shows how the SCC moves towards the right between the purity of the purified stream and the pinch purity interval, indicating that an ethanol surplus has been introduced to this region. However, for other purity intervals, the SCC moves towards the left since part of the initial surpluses has been moved to a higher purity by the new ethanol purification unit. The area reduction between the SCC and DCC in the region below the pinch is equal to the area increase above the pinch. The above observations indicate that the conditions for network feasibility stated in Section 3 are not violated. The effect of the changes made to the network is illustrated in Fig. 5d. There is a change from a system constraint on ethanol supply above the pinch to a system with ethanol surplus indicated by the large arrow in the second step (the new source at ethanol fraction of 0.96) of the diagram. The surplus generated above the pinch can be exchanged with the ethanol demands to decrease the need for fresh bioethanol product, resulting in a lower target. The new minimum bioethanol makeup flow rate is found by following the targeting procedure described above. Fig. 5e and f depict the pinched bioethanol networks with and without the purification unit, respectively.

The reduction in the total bioethanol makeup flow rate and the consequent reduction in the flow rate of the waste stream are clearly indicated by the arrows in Fig. 5e. The great reduction in the ethanol waste is obvious in the pinched surplus diagram in Fig. 5f, indicating the system is now utilising the available ethanol more efficiently. A remarkable effect of the purification unit is that the pinch is lowered to an ethanol content of $x_p = 0.0249$. This opens the opportunity to use source streams at ethanol content

from as high as 0.9960 to as low as 0.0249 to supply a demand at any purity in between, which was not allowed in the initial pinched system according to the first bioethanol integration criterion. The source streams from PPU-1 (892 t/y at 64.00% purity), CFG-2 (1437 t/y at 15.09% purity), WSU-2 (21,670 t/y at 91.52% purity) and RDY-2 (2049 t/y at 50.95% purity) can be exchanged without impurity concerns since they come from the last steps of the AX purification. However, it must be acknowledged that in principle, impurities in certain ethanol-containing streams could constrain their use. In this particular example of bioethanol and arabinoxylan co-production, the processes are not particularly sensitive such that the nature of the impurities is unlikely to impose significant constraints of this sort (although this may need to be verified experimentally for certain operations). The “impurities” (principally bran and protein) are similar in the various process streams and are relatively innocuous, and the intention is that all of them should end up ultimately in the DDGS.

3. Results and discussion

The final network design along with the flow rates and purities of the exchanged and waste streams are depicted in Fig. 7. These values represent the mass balance on ethanol also indicating that the fresh ethanol utility imported to the system is equal to the amount of ethanol going to wastewater treatment. Since the introduction of the purifier modifies the network significantly, the final design is different to that in Fig. 6. Note that the streams imported and from the sources, PPU-1, CFG-2, WSU-2, RDY-2 and SWU-2 at purity levels between 0.0249 and 0.9960 are combined to supply the demands TMU-1 and SWU-1 at the intermediate purity level of 70%. The source stream from SWU-2 is a poor ethanol stream and it is mainly used for dilution of other source streams with higher purity, thus saving fresh water. Recycling part of that stream containing AX would increase recovery in the bran purification steps (TMU-1, SWU-1). The bioethanol makeup required for the co-production of AX is now 2459 t/y. Thus, the integration of

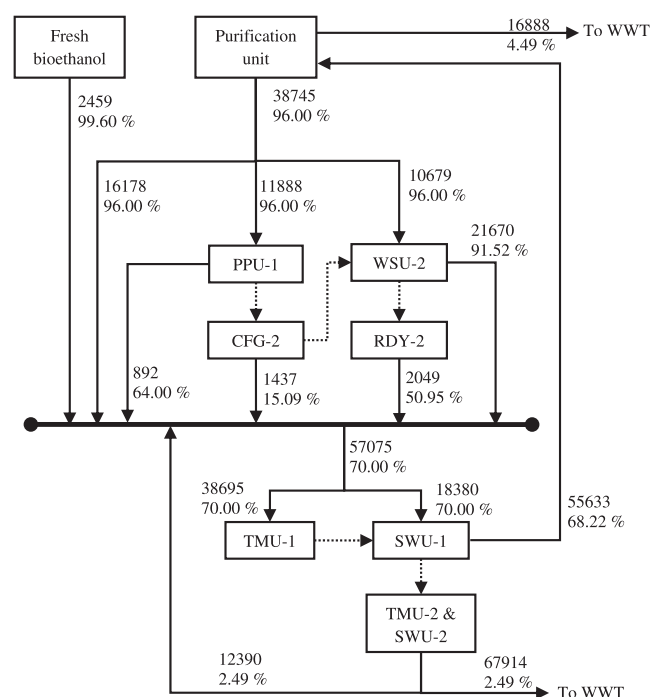


Fig. 7. The bioethanol exchange network design after integrating a purification unit. Flow rates in t/y.

Table 2

Summary of the impact of the various modifications from bioethanol network integration on fresh bioethanol product utilisation and economic indicators.

System	Fresh bioethanol (t/y)	Revenue losses (ME/y)	Avoided revenue losses (ME/y)	Column size (m ³)	Bare module capital cost (ME)	Net additional capital cost (ME)	Annualised additional capital cost (ME/y)	Net profit increase (ME/y)
Initial network	41,162	24.29	Base system	244	2.49	Base cost	Base	Base
Pinched (initial) network	12,512	7.38	16.90	244	2.49	0	0	16.90
With centralised purification column designed for increased capacity	2282	1.35	22.94	293	3.08	0.59	0.17	22.77
With additional purification unit in AX process				244 (initial)	2.49			
	2459	1.45	22.83	27 (additional)	0.381	0.381	0.11	22.72

the purification unit can save 10,053 t/y of bioethanol product additional to the savings from the first pinched system to make a total saving of 38,703 t/y. This means that the fresh bioethanol makeup required can be reduced by up to 94% from the 41,162 t/y in the initial network (Fig. 4).

Table 2 summarises the economic effects of the modifications to the initial network from the bioethanol integration using pinch targeting method. The revenue losses from bioethanol product utilisation are estimated assuming a bioethanol price of 590 £/t [8]. The distillation columns were simulated in Aspen Plus for preliminary sizing and their bare module capital cost was estimated by typical correlations available in the literature [42]. The capital cost was annualised using the same capital charge of 28% as in [8]. After the pinch targeting method is applied to the initial network, the biorefinery could avoid revenue losses of 16.9 ME/y without any change in the capital cost. However, purification of streams has been recommended from the pinch analysis as discussed before.

The system including the integration of a new purifier column (Fig. 7) was compared to the alternative system where the waste streams from SWU-1 and SWU-2 are sent back to the recovery and purification sections of the main bioethanol production process (Fig. 1). Table 2 shows that the total avoided losses in biorefinery revenues after bioethanol pinch analysis is 22.83 ME/y for the system with a new purifier column. The impact of installing a purification unit additional to the rectifier column in the main production process is a 15% increase in capital costs. This is less than the 24% cost increase for the installation of distillation columns designed for the increased capacity due to the processing of the waste streams from SWU-1 and SWU-2. In this alternative, the mass balance indicates that the fresh bioethanol surplus is reduced to 2282 t/y. Although the reduction is higher and therefore more revenue losses are avoided, the capital cost is also higher leading to a minimal difference in increased profitability between the two purification alternatives shown in Table 2. The impact on the capital costs is favourable for the installation of a new purification unit which also offers more process flexibility.

Another advantage of the final integrated network design in Fig. 7 is that the condensation of the stream from RDY-2 makes some heat available that can be used to preheat the AX stream to be dried to save drying heat duty. Therefore, the bioethanol pinch method illustrated here is not only helpful to devise integration strategies for increasing the ethanol use efficiency but can further be complemented with water and heat integration approaches for the production of a biorefinery design that is more efficient with respect to usage of bioethanol, water and heat.

4. Conclusions

A bioethanol pinch analysis method has been presented here as an effective tool for the design of bioethanol-based biorefineries

utilising feedstock more efficiently through integrated bioethanol exchange networks. The tool allows targeting for minimum fresh bioethanol consumption, thus preventing product and revenue losses. It also proved useful for evaluation of debottlenecking or improvement options. Integration principles and strategies helped to achieve an efficient, highly integrated bioethanol network. Combination of analytical-graphical and cost-benefit analysis can facilitate the whole bioethanol based biorefinery process synthesis and retrofit designs. The bioethanol pinch analysis approach could be adopted by other comparable product-based biorefineries.

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Chapter 3

Environmental sustainability

analysis of a wheat-based biorefinery

3.1 Preamble

Rigorous integration and life cycle assessment of biorefinery systems are required to ensure that their design and operation are more sustainable compared to its fossil-based counterparts or even competing biorefinery systems. Thus, planned and deliberate sustainable process design of biorefineries is necessary. This means using biomass efficiently to prevent the production of waste and emissions that can be a threat to the environment, while reducing the amount of land used to grow biomass feedstock. Energy should be used and produced efficiently, not only to reduce costs, but also to prevent the build up of carbon dioxide in the atmosphere and to preserve reserves of fossil resources.

Of all technological and conceptual developments in the last several decades, process integration has arguably made the largest practical contribution in increasing energy efficiency and minimising wastes and pollutants from industrial processes (Klemes et al., 2011). Thus, benefits from current process integration practice (e.g. heat and water integration methods) can be directly transferred to biorefinery design. However, the relevancy and importance of environmental sustainability for biorefinery development along with the distinctive multitude of options for biorefinery integration require careful assessment to select the configuration that offers the maximum environmental benefit. Life cycle assessment (LCA) has been used to assess the environmental sustainability of biorefineries, especially to evaluate energy and GHG balances of biofuel-driven biorefineries (Cherubini and Ulgiati, 2010; Dale et al., 2010; Wellisch et al., 2010; Sacramento-Rivero, 2011; Schaidle et

al., 2011). LCA allows accounting for direct and indirect impact from extraction and processing of raw materials, manufacturing, transportation and distribution, use, re-use, maintenance, recycling and final disposal and is a tool internationally accepted and standardised by the ISO 14040 standard (Guinée et al., 2002). LCA studies of biofuels have shown that, in addition to the use of fossil energy due to fertiliser application in biomass cultivation, the use of fossil energy for biomass conversion is also an important contributor to the overall environmental performance (Wellish et al., 2010). Thus, any improvement in biorefinery system designs that increase overall energy efficiency and reducing dependency on fossil energy by process integration tools will enhance the sustainability of biorefineries. The publication presented in this chapter emphasises this argument to evaluate the extent of the benefit from energy integration in a case study.

As with other countries in the European Union, the United Kingdom (UK) is adopting strategies for sustainable transportation by encouraging and mandating the use of biofuels, especially bioethanol and biodiesel (Renewable Fuels Agency, 2009). The availability of wheat in this country makes it an important feedstock for bioethanol. For instance, Europe's largest biorefinery is located in Teesside, UK and processes 1.2 million ton of wheat annually to produce 410 million litres of ethanol, 340 000 ton of DDGS and 340 000 ton of CO₂ (which is captured and purified for food and beverage use) (IEA Bioenergy, 2013). The publication presented in this chapter presents an environmental sustainability assessment of a whole wheat-based biorefinery in UK context.

3.2 Discussion of publication 2

The paper presents schemes for the utilisation of the whole wheat plant by coupling bioethanol production from grain starch fermentation and combined heat and power (CHP) production from straw gasification. Various synergies were explored including the use of DDGS (Dried Distillers Grains with Solubles) for utility supply using combustion or gasification technologies. The standalone bioethanol plant wherein the utility supply comes from conventional sources (natural gas and grid electricity) was evaluated using LCA in terms of global warming potential from GHG in a 100-year horizon (GWP₁₀₀), cumulative fossil primary energy demand

(CPE), eutrophication and acidification potential and abiotic resource depletion. The hot spots and main contributors to the life cycle impact are identified. Utilities (heat and electricity) were found to be the highest contributors within the process. It was also found that the bioethanol produced in this system might not be able to meet GHG emission reduction targets set by the EU Renewable Energy Directive by 2020 (European Union, 2009).

With the aim of reducing the fossil-based energy use and GHG emissions and increasing the life cycle energy efficiency, five alternatives for an integrated biorefinery were evaluated in terms of global warming potential from GHG and cumulative fossil primary energy demand. The results were compared to the standalone bioethanol plant to establish the benefits of the integrated schemes. The savings with respect to a reference fossil-based system producing the same amounts of energy were also estimated. An alternative integrated scheme with bioethanol energy requirements met by straw-based CHP and DDGS sold as animal feed offers GHG reduction of 85% and CPE savings of 97% with respect to the reference system. Another alternative scheme using straw-based CHP and heat from DDGS combustion achieves GHG reduction of 63% and CPE saving of more than 100%.

Overall, the holistic process integration and LCA framework developed has proved to be effective to support utility integration in biofuel biorefineries in order to increase overall energy efficiency and environmental sustainability. The work reinforces the argument of the essential role of process integration combined with the assessment of alternatives through life cycle approaches to produce sustainable biorefinery designs.

Methodological aspects

As in the previous chapter, some details on the methodologies, tools and assumptions are clarified in this section. The development of the process models was not the purpose of this publication, only LCA modelling is built on top of existing process and wheat cultivation models. All the LCA calculations were performed in Excel spreadsheets using data extracted as indicated in the paper presented in this chapter. It is worth mentioning that the LCA study undertaken and presented in the publication of this chapter was the basis for the assimilation of LCA concepts, which

were taken further into the combined methodology for economic and environmental impact assessment (presented in Chapters 5 and 6). The origin of models and some data is clarified as follows.

As mentioned in the paper, mass and energy balances of the processes were linearly scaled-up from existing spreadsheet-based models. The model for the bioethanol plant was previously developed by Sadhukhan et al. (2008) and also described by Misailidis et al. (2009). In the case of the combined heat and power (CHP) plants, the amounts of power and heat were estimated in a spreadsheet by scaling-up the results from the study carried out by Ibrahim (2010), which is based on the simulation framework of Sadhukhan et al. (2009). These previous works present the details of the process models and were carried out within the department of Process Integration at The University of Manchester. The mass and energy flows for the case study concerning this thesis are given in Figure 2, Table 2 and Table 8 of the publication presented in this chapter. More detailed balance tables are provided in Tables A to C of the Appendix. The basis for calculation was the processing of 1.2×10^6 Mg y^{-1} of wheat grain and the corresponding amount of available straw.

In the case of the wheat cultivation system and the environmental impact factors for the related inventories (fertilisers, machinery, diesel, pesticides, etc.), the models developed by Williams et al. (2006) were adopted. The models are described in detail in the cited reference and are available as a spreadsheet (Cranfield University, 2013). The activities or processes from the cultivation system that were taken into account for the case study, for which inventory data was extracted from the aforementioned models, are depicted in Fig. 2 of the publication in this chapter. The final results of the LCA of the cultivation system are presented in Table 3.

It is assumed that the biorefinery is located within the radius of the wheat cultivation system. The calculation of such radius is considering the amount of land used for the cultivation of the wheat used in the biorefinery and assuming a circular shape, as explained in the paper (resulting in a value of 25 km, section 3.2). For raw materials required for the bioethanol process, 120 km is an average freight travelling distance in the UK. This value results from considering an average of 12 km per tonne of goods transported and assuming a freight carrying capacity of 10 tonnes (Allen and Browne, 2010).

In the case of allocation of impacts by economic value between wheat and grain (Williams et al., 2006) and between bioethanol and DDGS (Sadhkhan et al. (2008), the prices used were in line with the corresponding references. It is recognised that these values are not fixed and evolve with time. Although sensitivity analysis was not a goal in this case study, it is recommended to evaluate the effect of uncertainty on the results of the study. The limitations of the studies presented in this thesis are discussed in Chapter 7 along with some recommendations to address such limitations.

The greenhouse gas (GHG) emissions and cumulative fossil primary energy (CPE) were compared between bioethanol and gasoline. This comparison was carried out on an energy basis, i.e. assuming that 1 MJ of bioethanol energy content replaces 1 MJ of gasoline energy content. This approach is convenient since the common service that these products provide is energy. Cherubini and Ulgiati (2010) have reported GHG emissions in the basis of 1 km travelled in a car using the bioethanol specific consumption of 2.45 MJ km^{-1} . This could be a basis that is more practical and easy to understand in daily life. The best system studied in the publication presented in this chapter produces bioethanol with a GHG emissions factor of $12.63 \text{ g CO}_2\text{-eq MJ}^{-1}$. This value is translated into $30.9 \text{ g CO}_2\text{-eq km}^{-1}$ by using bioethanol as fuel, which is about 84% lower than the value of $198 \text{ g CO}_2\text{-eq km}^{-1}$ from using gasoline (factor for gasoline reported in Cherubini and Ulgiati, 2010). However, actual fuel efficiency is subject to the specific characteristics of the engine type, car model, age, mileage and the conditions of fuel use such as the speed, the ambient temperature, etc. Testing fuel efficiency in every car engine is impractical and thus the comparison on a MJ per MJ basis is a reasonable and more convenient approach. Alternatively, a sensitivity analysis is recommended to determine the range of replacement ratios between bioethanol and gasoline and the corresponding range of savings on GHG emissions and CPE.

Publication 2: Martinez-Hernandez, E., Ibrahim, M.H., Leach, M., Sinclair, P., Campbell, G.M., Sadhukhan, J., 2013. *Environmental sustainability analysis of UK whole-wheat bioethanol and CHP systems*. Biomass and Bioenergy 50, 52–64.

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Environmental sustainability analysis of UK whole-wheat bioethanol and CHP systems

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ABSTRACT

The UK whole-wheat bioethanol and straw and DDGS-based combined heat and power (CHP) generation systems were assessed for environmental sustainability using a range of impact categories or characterisations (IC): cumulative primary fossil energy (CPE), land use, life cycle global warming potential over 100 years (GWP₁₀₀), acidification potential (AP), eutrophication potential (EP) and abiotic resources use (ARU). The European Union (EU) Renewable Energy Directive's target of greenhouse gas (GHG) emission saving of 60% in comparison to an equivalent fossil-based system by 2020 seems to be very challenging for stand-alone wheat bioethanol system. However, the whole-wheat integrated system, wherein the CHP from the excess straw grown in the same season and from the same land is utilised in the wheat bioethanol plant, can be demonstrated for potential sustainability improvement, achieving 85% emission reduction and 97% CPE saving compared to reference fossil systems. The net bioenergy from this system and from 172,370 ha of grade 3 land is 12.1 PJ y⁻¹ providing land to energy yield of 70 GJ ha⁻¹ y⁻¹. The use of DDGS as an animal feed replacing soy meal incurs environmental emission credit, whilst its use in heat or CHP generation saves CPE. The hot spots in whole system identified under each impact category are as follows: bioethanol plant and wheat cultivation for CPE (50% and 48%), as well as for ARU (46% and 52%). EP and GWP₁₀₀ are distributed among wheat cultivation (49% and 37%), CHP plant (26% and 30%) and bioethanol plant (25%, and 33%), respectively.

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1. Introduction

In 2008/2009, UK surplus wheat (dry basis) was around 3,900,000 Mg available for the production of bioethanol [1]. Alongside, 3500 kg ha⁻¹ of accompanying wheat straws (dry basis) were produced, 60% of which, after incorporating the rest into the soil for retaining the soil nutrients, could have been made available for the generation of combined heat and power (CHP) [2]. In the UK, there is around 5,000,000 Mg y⁻¹ of straw available for bioenergy purposes, 54% coming from

wheat, after accounting for its other current uses [3]. Transport is the main energy consuming sector in the UK, accounting for a quarter of the UK domestic energy use and GHG emissions. 93% of those emissions come from road vehicles [4]. In order to reduce emissions and energy imports, the target is to introduce 5.26% of renewable fuels into the transport fuel by 2013/2014 [5]. To meet this bioethanol demand, a production capacity of 1 billion L will be required in the UK by the year indicated. The amount of excess wheat available in the UK could provide 1.62 billion L y⁻¹ of

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bioethanol (according to bioethanol process studies in Ref. [6]). The target fraction for electricity from renewable resources is set at 10% by 2010 and 30% by 2020 (2% from small-scale generation) [7]. This implies that 48.2 PJ y^{-1} of electricity is required from biomass by 2010 [8]. The excess straw available in the UK (at 14.6 MJ kg^{-1}) can supply 29.2 PJ y^{-1} of electricity.

The EU Directive 2009/28/EC on Renewable Energy has imposed a constraint on biofuel systems that only those saving 60% GHG emissions in comparison to the fuel they replace will be eligible for consideration for the 2020 target of 10% renewable energy in transport [9]. Whilst achieving this target from the bioethanol production alone can be an important consideration, integrated energy systems have greater potential in improving overall sustainability. The utilisation of rape seed to produce a range of products, biodiesel from the oil, heat from straw, heat and gas from glycerol and rape cake as animal feed has been investigated to achieve 60% emission reduction target [10]. Their studies have demonstrated the sustainability of indigenous biofuels in Ireland in comparison to equivalent biofuel imports from other resources [10–12]. A comprehensive comparison amongst various potential renewable energy systems in the UK has been shown by a streamlined LCA approach [13]. An excellent overview of environmental impact analysis of the large scale deployment of dedicated bioenergy crops (e.g. short rotation coppice (SRC) willow and poplar, miscanthus) and biomass for biofuels (e.g. wheat, sugar beet, oilseed rape) in the UK has also been reported [14]. A range of GWP_{100} (as $\text{CO}_2\text{-eq}$) values between 41 g MJ^{-1} and 80 g MJ^{-1} from bioethanol plants using different feedstock (sugar cane, sugar beet, wheat, corn), with corresponding potential GHG reductions in a range of 10–53% was shown [15]. With a similar approach, the life cycle assessment (LCA) of bioethanol and CHP production systems from wheat straw, considering additional aspects like crop residue removal and decrease in grain yields has also been presented [16]. The calculations showed that the use of crop residues in a biorefinery reduced GHG emissions by about 50% and fossil energy demand by more than 80%. The effect of the processing scale and different allocation methods (economic, physical and by system expansion) have been analysed within the Sweden context [17]. The results showed that the differences between various scales are small and suggested system expansion as an appropriate allocation method. A GWP_{100} (as $\text{CO}_2\text{-eq}$) of 43.5 g MJ^{-1} from a wheat-based large scale bioethanol facility based on economic allocation was presented.

The above studies mainly focus on the analysis of key contributing factors in LCA of bioenergy systems from different feedstock [10–18]. However, the trend is to make comparisons among them but give less attention to the improvement of environmental performance on a specific system from their current status as in the case of bioethanol plants. Additionally, the LCA of integrated energy systems in the UK is under-explored. It is also imperative to undertake such studies in the appropriate context and present the assumptions, results and validations in the most transparent and coherent way.

The current work explores, through the life cycle methodologies, the improvement in environmental sustainability from wheat bioethanol to the whole-wheat bioethanol plants, in which the DDGS and the wheat straws are also used to generate CHP, thereby enhancing the renewable energy mix

Table 1 – Common substances and characterisation factors for impact categories used in this study (per kg).

Substance	GWP_{100} ($\text{CO}_2\text{-eq}$) (kg) [20]	AP ($\text{SO}_2\text{-eq}$) (kg) [21]	EP ($\text{PO}_4^{3-}\text{-eq}$) (kg) [21]
CO_2	1		
CH_4	25		
N_2O	298		
CO	1.9		
NO_x (not N_2O)		0.7	0.13
SO_x		1	
H_2SO_4		0.65	
NH_3		1.88	0.33
NO_3^-			0.42
PO_4^{3-}			1

into the system. Building upon bioenergy system overviews presented in literature [10–29], a detailed evaluation of the UK wheat bioethanol and lignocellulosic CHP plants was performed in the context of environmental sustainability. The life cycle impact (LCI) methods were used with impact factors from individual substances extracted from various sources [19–29], amongst which the more relevant ones are presented in Table 1. For various energy carriers, e.g. natural gas, electricity, diesel, etc., the factors from Ref. [19] were used.

The specific objectives of this study include:

- 1) Assess the environmental impact of the UK wheat bioethanol plant [6] as a stand-alone system as well as a whole-wheat system integrated with wheat straw CHP plant [30] using cumulative primary (fossil) energy (CPE), land use, global warming potential in a horizon of 100 years (GWP_{100}), acidification potential (AP), eutrophication potential (EP) and abiotic resources use (ARU) as IC.
- 2) Establish the marginal benefits in terms of GWP_{100} and primary energy savings, compared to the fossil resources to be replaced, e.g. natural gas for heat and electricity and gasoline for bioethanol.
- 3) Study the relative LCI of DDGS as a commodity to the production of heat and CHP, compared to its usage as animal feed.

2. System definition

Fig. 1 depicts the following alternatives evaluated through life cycle methodologies:

- 1) Stand-alone bioethanol plant; wheat bioethanol and straw CHP to grid system.
- 2) DDGS as a source of heat for wheat bioethanol plant.
- 3) DDGS as a source of CHP for wheat bioethanol plant.
- 4) Straw-based CHP plant supplying energy to bioethanol plant and DDGS as an animal feed.

Additionally, alternative 5 is a combination of the cases in 2 and 4, wherein selling of DDGS is also considered.

The basis of the conversion plants is $12,000,000 \text{ Mg y}^{-1}$ of wheat grain and the corresponding amount of excess straw

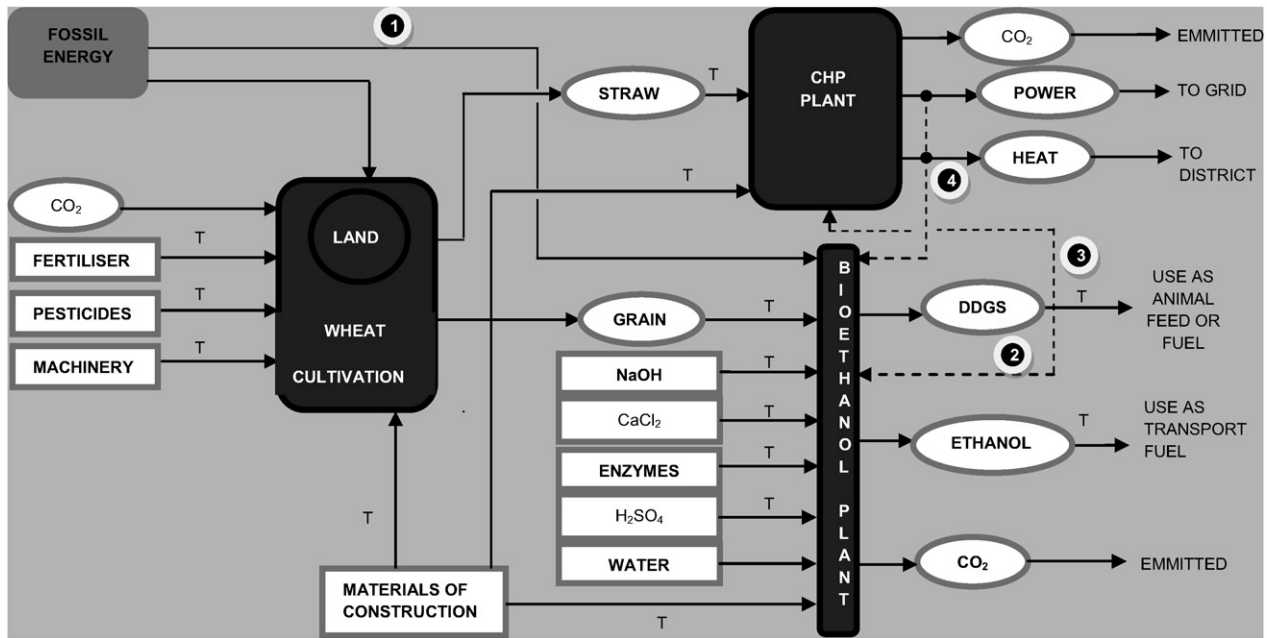


Fig. 1 – The system evaluated. T: indicates transportation of materials. Dashed lines indicate the integration alternatives explored.

available, 360,000 Mg y⁻¹ (after assuming retention of the straws cultivated in the soil of 40% to maintain the soil's nutritional value). The yields and energy contents of products are reported in Table 2.

The boundaries of each subsystem include the farm and the plant gates for LCA. The allocation between the grain and the straw is by their economic values. For the conversion subsystems, three activities were separately evaluated and combined: LCI of materials of construction, plant operation, and transportation. The spreadsheet-based wheat bioethanol process model developed for technical analysis and economic feasibility [6] has been adopted. The results of simulation of biomass integrated gasification combined cycle (IGCC) plant for CHP generation in Aspen Plus were extracted for LCA [30].

The end use of ethanol is combustion as transportation fuel and of DDGS is in animal food processing in the base case, or as fuel for energy production in other cases. The electricity and heat generated from either the straw or from the DDGS were used within the bioethanol plant and added to adjacent grid connection and district heating system. Complementary energy such as electricity and natural gas is taken from the grid where necessary.

The LCI of individual co-production was allocated based on associated activities and operations. For shared facilities, this allocation was done by economic values. Different common functional units (unit mass of dry matter (DM) of product, unit energy, year and in the case of wheat cultivation, ha) were used for comparisons.

Table 2 – Summary of yields (in dry matter basis) of wheat cultivation and bioethanol and CHP generation plants.

Subsystem	Product	Yield	Unit	LHV ^a (MJ kg ⁻¹)
Wheat cultivation [19]	Wheat	6960	kg ha ⁻¹	18.6
	Straw	3490	kg ha ⁻¹	14.6
Bioethanol plant [6]	Ethanol	0.34	kg kg ⁻¹ (wheat basis)	26.7 [13]
	DDGS	0.25	kg kg ⁻¹ (wheat basis)	18.2
	Electricity	1.06	kWh kg ⁻¹ (straw basis)	
Straw CHP plant [30]	Heat	0.567	kWh kg ⁻¹ (straw basis)	
	Efficiency	40	%	

a LHV: lower heating value.

3. Life cycle assessment

3.1. Wheat cultivation

The LCI data of wheat cultivation in the UK (Fig. 2) were extracted from Ref. [19]. Various applications of nitrogen fertiliser are generally made followed by sprayings of pesticides (2 doses assumed). The grain (with moisture content of 15–18%) once harvested is dried to avoid deterioration during storage and then is transported to the grain store. A mass fraction of the straws of about 40% are chopped and ploughed back to the soil to retain and improve the nutrient balance, soil fertility and organic carbon content. The rest is baled and used within the farm or is sold for other purposes [2]. The wheat yield of 6960 kg ha⁻¹ and the corresponding straw yield of 3500 kg ha⁻¹ were determined (in dry basis) using 200 kg ha⁻¹ of nitrogen fertiliser. Urea mass fraction of 20% and the rest

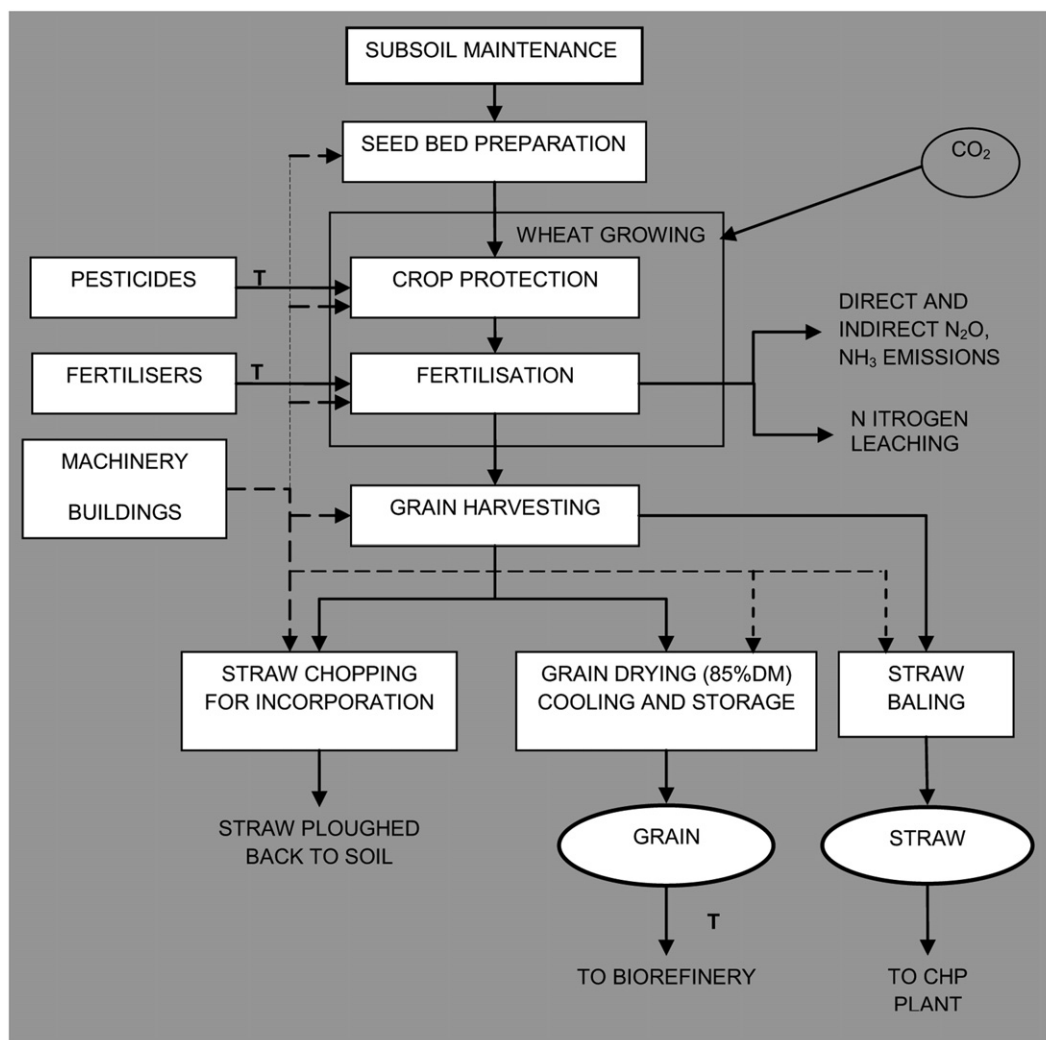


Fig. 2 – The main activities in the UK cultivation system. Every activity implies machinery operations with its inherent energy use and environmental impact for manufacturing, housing and transportation. Transportation is denoted by T. DM: dry matter.

ammonium nitrate were assumed as fertilisers [19]. A total CO_2 binding of 10.5 Mg ha^{-1} by photosynthesis by the wheat plant was used [24].

The GHG emissions during the field operations are primarily from the usage of energy and fertilisers. N_2O emissions from the nitrogen fertiliser and organic matter decomposition in soil produce impacts [15]. Direct field emissions from nitrogen fertiliser and organic matter decomposition in soil and indirect field emissions from nitrogen volatilisation, and deposition of nitrogen volatilised as $\text{NH}_3 + \text{NO}_x$, were determined based on the estimated factors by IPCC, Tier 1 [22].

The total CPE and allocation of impacts to grain and straw were predicted following the default relative economic value factor of straw to grain of 0.05 [19] and depending on 40% of straws incorporated in the soil in this study. The activities up to grain harvesting were common since the straw production (baling) occurs only after grain harvesting (Fig. 2). The resulting allocation values in different functional units are given in Table 3.

The results are assimilated for a range of activities, Fertilisers and Pesticides (F&P), Field Operations (FO), Grain Conditioning (GC), and Direct and Indirect Field Emissions (FE) in Fig. 3. The CPE and GWP_{100} impacts from various wheat production activities are compiled in Table 3. The output raw energy available in the form of grain and straw (calculated from LHV in Table 2) gives a land productivity of 129.5 GJ ha^{-1} from an input CPE of $18.967 \text{ GJ ha}^{-1}$ (Table 3). This leads to an energy ratio, $E_{\text{ratio}} = \text{output LHV}/\text{input CPE}$, of 6.82 from the wheat cultivation system.

The GWP_{100} impact from the field is essentially due to N_2O releases. The field emissions are also the most important factor to eutrophication potential (99.9%, not shown in Fig. 3) due to NO_3^- leaching and NH_3 emissions. Regarding acidification potential, it is dominated by NH_3 emissions.

As illustrated, FE and fertiliser production are the hot spots in the LCA of wheat production. Both are related to the nutrient balance in the soil which is still an issue to address in agricultural systems. Decreases in the application of nitrogen

Table 3 – Allocation of CPE and environmental impacts from wheat cultivation.

Product	Functional unit	CPE (MJ)	GWP ₁₀₀ (CO ₂ -eq) (kg)	EP (PO ₄ ³⁻ – eq) (kg)	AP (SO ₂ -eq) (kg)	ARU (Sb-eq) (kg)
Grain	ha	18,335	3426	16.1	15.8	10.8
Straw	ha	632	77	0.2	0.2	0.30
Total	ha	18,967	3503	16.3	16.0	11.1
Grain	Mg	2634	492	2.3	2.3	1.5
Straw	Mg	181	22	0.1	0.1	0.1
Grain	y	3.16 PJ	591,000 Mg	2770 Mg	2720 Mg	1850 Mg
Straw	y	0.109 PJ	13,300 Mg	41.7 Mg	42.5 Mg	52.6 Mg
Total	y	3.27 PJ	604,000 Mg	2810 Mg	2760 Mg	1910 Mg
Land use		Grade 2 ha	Grade 3a ha	Grade 3b ha	Grade 4 ha	
Total	y	151,685	172,370	186,159	193,054	
Grain	Mg	0.13	0.14	0.16	0.16	

fertilisers can improve the overall environmental performance of wheat production and subsequent processing.

3.2. Wheat bioethanol system

The wheat to bioethanol process model comprising hammer milling, liquefaction, saccharification, fermentation, centrifugation, ethanol recovery and drying as the main units [6] was used for the generation of mass and energy balance presented in Fig. 4. The simulation is based on the processing of the total wheat grain produced from cultivation into 404,000 Mg y⁻¹ of ethanol, 361,000 Mg y⁻¹ of CO₂ (emitted to atmosphere), and 295,000 Mg y⁻¹ of DDGS. The plant operates for 330 days a year and the plant life was assumed to be 10 years. Water recovered from the distillation columns is recycled into the process. For the base case, natural gas is used to supply the heat required by the fermentation, distillation and drying.

The various substances consumed, α -amylase, CaCl₂ (liquefaction), glucoamylase, H₂SO₄ conc. (saccharification) and yeast (fermentation) in the bioethanol production are presented in Table 4. NaOH is also required; a detailed inventory

of its production was included [27]. Yeast was assumed to have equivalent LCI as glucoamylase. Additional emissions were accounted for the transportation of the substances from their production gate to the bioethanol plant assuming a distance of 120 km. Wheat is assumed to be transported from the farm gate to the bioethanol plant located within a radius of 25 km estimated from the total land use (grade 3a in Table 3). A mass fraction of 30% of all materials transported by lorry and the rest by rail [19] was assumed to determine the energy requirements and environmental impact from transportation.

The main materials of plant construction considered were steel and concrete assuming mass fractions of 70% and 30%, respectively. The steel requirement was determined from the preliminary sizing of the key equipment made up of tanks and columns, and other vessels according to Refs. [31–33]. Residence time used in the calculations and amounts of steel are presented in Table 5. A detailed inventory for stainless steel grade 316 [25] was used to determine the environmental impact from the amounts in Table 5. At the end of the life of the plant the steel can be recycled, thus considered a credit within the inventory. The emissions from concrete production were estimated from that of cement [26]. The LCI was

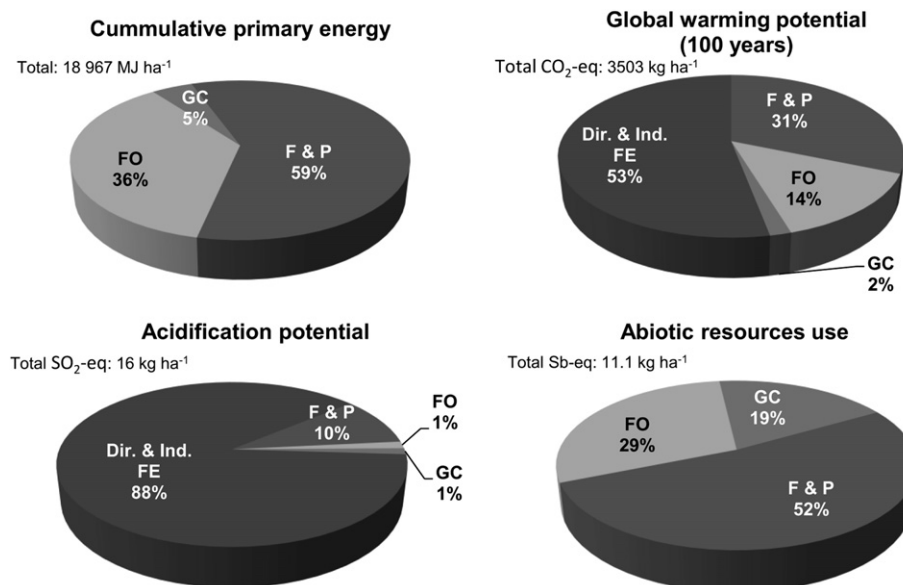


Fig. 3 – Distribution of CPE and main environmental impact categories from wheat cultivation. FO: Field Operations, F&P: Fertilisers and Pesticides, Dir. & Ind. FE: Direct and Indirect Field Emissions, GC: Grain Conditioning.

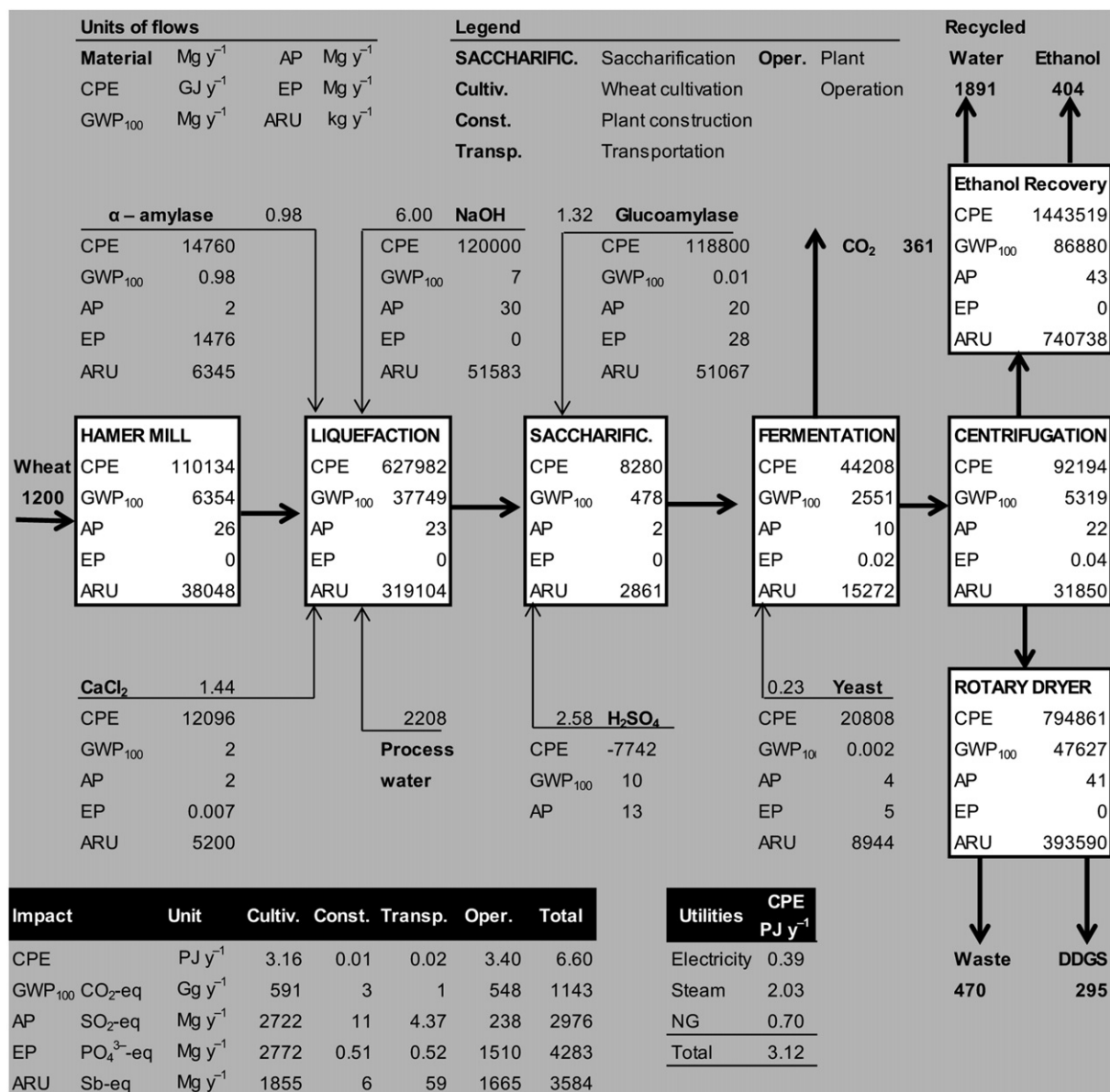


Fig. 4 – Material and energy balances and environmental impacts associated with every stream and unit operation in the wheat bioethanol plant.

increased by 20% and 10% for buildings and general structural elements in the facility and for the decommissioning of the plant at the end of life, respectively. A distance of 120 km was assumed for the transportation of materials of construction, as before.

Fig. 4 depicts the environmental impact and CPE flows for the cradle to the bioethanol plant gate subsystem including

wheat cultivation, transportation and plant operation and construction. The construction stage represents only a small fraction (1% or less) of the total environmental impact of the plant.

The impact from wheat grain production is the maximum, followed by bioethanol process operation, transportation and materials of construction in all the IC. The GHG emission from

Table 4 – Substances and environmental impacts data (per kg).

Substance	CPE (MJ)	GWP ₁₀₀ (CO ₂ -eq) (kg)	EP (PO ₄ ³⁻ – eq) (kg)	AP (SO ₂ -eq) (kg)	Ref.
α-amylase	15	1	0.0015	0.005	[28]
Glucoamylase	90	7.7	0.0215	0.023	[28]
CaCl ₂	8.40				[29]
H ₂ SO ₄ Conc.	–3	0.004		0.005	[29]

Table 5 – Main equipment and amount of steel required assuming cylindrical shapes.

Unit	RT ^a [31] (h)	Capacity (m ³)	Steel ^b (kg)
Liquefaction	1	364	10,779 (1%)
Saccharification	5	2020	33,810 (4%)
Fermentation (10 tanks)	68	27,475	420,294 (52%)
Centrifugation	1	1083	22,312 (3%)
Ethanol recovery	3 columns	5188	123,154 (15%)
Rotary dryer	1	1083	22,312 (3%)
Condensate tank	6	14,100	123,479 (15%)
Ethanol tank	24	4369	56,541 (7%)
TOTAL			812,682

a RT: Residence time.

b Numbers in brackets are mass fractions of the total amount.

the process is caused from the use of energy and fermentation. The GWP₁₀₀ (as CO₂-eq) from cradle to the bioethanol plant gate represented a value of 0.95 kg kg⁻¹ for the UK wheat grain processed, or 6.78 Mg ha⁻¹ (based on grade 3a in Table 3).

Based on the LHV and yields of ethanol and wheat in Table 2, an annual energy production (E) of 10.8 PJ y⁻¹ through ethanol is obtained from 22.3 PJ y⁻¹ of cumulative primary energy. In terms of the land use, the energy conversion from wheat to bioethanol translates to a land productivity of 62.7 GJ ha⁻¹ y⁻¹ (based on land grade 3a in Table 3). The ethanol distillation columns and rotary dryer are the most energy consuming processes within the bioethanol plant, indicating points for potential improvement. Replacing natural gas-based energy and electricity from the grid with renewable CHP using integrated systems can further enhance the environmental sustainability of bioethanol production and usage, discussed later.

The economic values assigned in the study [6] have been taken as a basis for the allocation of LCI to ethanol and DDGS. The total environmental impact under each category for each product was determined by the allocation factor of the product (AF) multiplied by the total environmental impact from common unit operations (CEI), plus the environmental impact from the unit operations used in the final recovery of that particular product (REI); i.e.: AF × CEI + REI. The allocation factor was calculated from the ratio of the value flow of the product (mass flow multiplied by economic value) divided by the sum of value flow of all products. This results in the factors of 0.962 and 0.038 for ethanol and DDGS, respectively. The LCI allocation to bioethanol and DDGS by economic values is presented in Table 6.

Table 7 presents cradle-to-grave GWP₁₀₀ of wheat bioethanol production, including combustion, CO₂ binding and

Table 7 – Results of GWP₁₀₀ (CO₂-eq) and corresponding savings from the use of bioethanol as transport fuel and DDGS as animal feed, respectively.

	Unit	Ethanol	DDGS
Allocation from production	kg kg ⁻¹	2.62	0.29
Ethanol combustion		1.91	–
Transportation		0.01	0.001
Total GWP₁₀₀		4.5	0.29
CO ₂ binding by wheat		–3.16	–0.12
Net GWP₁₀₀		1.38	0.17
	g MJ ⁻¹	51.6	–
Energy produced	MJ kg ⁻¹	26.72	–
Total CPE		13.94	3.25
E _{ratio}	–	1.92	–
Reference values	–	Gasoline	Soy meal
GWP ₁₀₀	g MJ ⁻¹	84.6 [14]	–
	kg kg ⁻¹	–	0.726 [35]
E _{ratio}	MJ MJ ⁻¹	0.84 [14]	–
CPE	MJ kg ⁻¹	–	4.13 [34]
GWP₁₀₀ reduction	%	39	72
CPE savings	%	56	21

product transportation. By considering the impact allocation to ethanol and DDGS by their economic values, the reduction in GWP₁₀₀ impact of 39% is obtained in comparison to gasoline system. From the corresponding CPE (13.94 GJ Mg⁻¹) and the energy produced from ethanol (Table 2), the energy ratio for bioethanol production is E_{ratio} = 1.92. This ratio reported for the production of gasoline is 0.84 [14]. Thus, energy saving of 56% can be estimated. On the other hand, considering that 1 kg of DDGS can replace 0.8 kg of soy meal for animal feed [34] and the corresponding GWP₁₀₀ of 0.726 kg kg⁻¹ soy meal [35], 72% of GHG emissions can be avoided by the replacement of soy meal in animal feed. A potential energy saving of 21% was estimated from the use of DDGS as animal feed.

The GWP₁₀₀ (as CO₂-eq) from the production of bioethanol from the UK wheat determined (51.6 g MJ⁻¹) fits within the range of (40.8–79.6) g MJ⁻¹ given in Ref. [15] with potential GWP₁₀₀ reduction by 10–53%. The resulting value is also comparable with 43.5 g MJ⁻¹ from bioethanol production in Ref. [17] and 44 g MJ⁻¹ reported in Ref. [14], based on similar system definition and economic allocation.

3.2.1. Sensitivity analysis

Sensitivity analysis was carried out by variation of the percentage of renewable electricity in the electricity mix, percentage of renewable fuel in transportation fuels and nitrogen fertilisation rates. The impact sources affected by these parameters are: transportation, field operation and drying. The biogenic carbon capture is not affected by these parameters

Table 6 – LCI allocation to ethanol and DDGS by economic value (from cradle to the plant gate).

Product	Functional unit	CPE (PJ)	GWP ₁₀₀ (CO ₂ -eq) (Mg)	AP (SO ₂ -eq) (Mg)	EP (PO ₄ ³⁻ – eq) (Mg)	ARU (Sb-eq) (Mg)
Ethanol	y	5.64	1,057,711	2826	4122	3098
DDGS	y	0.96	85,598	150	161	486
Total	y	6.60	1,143,309	2976	4283	3584
Ethanol	Mg	0.00001394	2.62	0.01	0.01	0.0077
DDGS	Mg	0.00000325	0.29	0.001	0.001	0.0016

and therefore CO₂ binding and carbon emissions from end use of products are not changed. The initial UK electricity mix is 43.3% from natural gas, 32.9% from coal, 2.6% from fuel oil, 18.2% from nuclear energy and 3% from renewable energy [19]. It was assumed that the biofuels replace an equivalent amount of fossil fuels and that the use of biofuel results in at least 50% reduction in CPE and GWP₁₀₀ with respect to fossil fuels. The results of sensitivity analysis are shown as follows:

- 10% increase in renewable electricity in the electricity mix increases CPE by 0.02 PJ y⁻¹ and reduces GWP₁₀₀ by 1144 Mg y⁻¹, EP by 0.005 Mg y⁻¹, AP by 2.07 Mg y⁻¹ and ARU by 17.7 Mg y⁻¹.
- 10% biofuel in transportation fuels increases CPE by 0.07 PJ y⁻¹ and reduces GWP₁₀₀ by 3382 Mg y⁻¹, EP by 0.10 Mg y⁻¹, AP by 11.2 Mg y⁻¹ and ARU by 5.86 Mg y⁻¹.
- 10% reduction in nitrogen fertilisation rates increases CPE by 0.14 PJ y⁻¹ and reduces GWP₁₀₀ by 33,351 Mg y⁻¹, EP by 142 Mg y⁻¹, AP by 346 Mg y⁻¹ and ARU by 0.08 Mg y⁻¹.

Major changes came from the variation in nitrogen fertilisation rates. The estimated field emissions using IPCC guidelines are another source of uncertainty.

3.3. Wheat bioethanol and straw CHP to grid system

The biomass IGCC-based CHP system has been technoeconomically proven to be competitive and environmentally superior to equivalent fossil-based (e.g. natural gas-based) CHP systems [30] and their implementation seems to be a reality [36]. The LCA of a process simulated in Aspen Plus by Sadhukhan et al. for the processing of 5.44 Mg d⁻¹ straw (with moisture and ash mass fractions of 8.5% and 8.61%, respectively, and LHV of 14.6 MJ kg⁻¹) into the production of 241 kW of electricity and 129 kW of waste heat, was undertaken [30]. The scaled up LCA results in terms of CPE and GWP₁₀₀ corresponding to 361,000 Mg y⁻¹ of straw processing into 1.38 PJ y⁻¹ of electricity and 0.737 PJ y⁻¹ of heat generation, and thereby whole system LCI results under all five IC are presented for the base case (alternative 1 in Fig. 1).

The GWP₁₀₀ from the straw-based CHP plant is mainly from the operation (98%) and the rest from the straw production and transportation and the plant construction. This impact mainly results from the emissions of the exhaust gas from the combustion of the syngas from straw gasification, made up of CO₂ (molar fraction of 25%), nitrogen (molar fraction of 62%) and steam (molar fraction of 13%) in the cases under consideration. However, by considering CO₂ fixation by straw (Carbon mass content of 36.6%) there is a credit of 1.34 Mg Mg⁻¹. Then, the net GWP₁₀₀ (as CO₂-eq) is reduced to 18 g kWh⁻¹. Thus, around 94% reduction in GHG emissions can be achieved by the CHP generation from wheat straw with respect to equivalent production of CHP from natural gas [19]. Alternative to gasification is the combustion of straw to produce heat and/or electricity. The electricity-only system has been analysed with the plant gate as system boundary and taking into account the CO₂ balance between that released by the processing and combustion and that fixed by the wheat plant [13]. Another conversion alternative is the wheat straw-based bioethanol and acetic acid system with lignin supplying CHP.

However, wheat straw can be interchangeably used between CHP and bioethanol production, without any difference in environmental impacts.

Unlike the bioethanol plant, the construction stage in wheat straw CHP system becomes important in the case of CPE (28%) and AP (25%), respectively. Transportation also has impact towards ARU (35%). For the other IC, the wheat straw cultivation incurs the maximum impacts, contributing by 66% to CPE, 68% to AP and 65% to ARU, respectively. Plant operation contributes the most to EP (98%).

Table 8 compiles the results of bioenergy production from the base case system (alternative 1), wheat bioethanol and DDGS as animal feed; and straw-based CHP to grid. The following analysis is done for the system as a whole without any allocation of impacts. The net bioenergy produced is 12.9 PJ y⁻¹, 84% of which in the form of ethanol and the rest in the form of CHP. Therefore, the bioenergy harvested from the land cultivated after conversion is 74.9 GJ ha⁻¹ y⁻¹. The E_{ratio} obtained is 1.91. The CPE requirements by the whole-wheat cultivation, bioethanol plant operation and transportation and construction of the wheat bioethanol and CHP system are 3.27 PJ y⁻¹ (Table 3), 3.40 PJ y⁻¹ (Fig. 4), 0.067 PJ y⁻¹ and 0.041 PJ y⁻¹, respectively. The CPE to produce the equivalent amount of energy and soy meal corresponds to 12.9 PJ y⁻¹ from gasoline (E_{ratio} = 0.84 [14]), 1.1 PJ y⁻¹ from heat generation from natural gas boiler (E_{ratio} = 0.7, assumed), 4.4 PJ y⁻¹ from electricity mix (3% of renewable mix in the current UK context), and 0.97 PJ y⁻¹ from soy meal production (Tables 7 and 8). This gives a total CPE of 19.37 PJ y⁻¹ with an overall E_{ratio} = 0.66. Therefore, about 65% energy savings can be achieved from the whole bioenergy system.

In the cradle to product utilisation (ethanol combustion) analysis of the whole base case (wheat bioethanol and straw CHP to grid) system, the total GWP₁₀₀ (as CO₂-eq) is calculated as the sum of that from the whole-wheat cultivation (Table 3), wheat bioethanol plant operation (Fig. 4), straw CHP plant operation, total transportation (4110 Mg y⁻¹), plant construction (4910 Mg y⁻¹) and ethanol combustion (at 1.9 Mg Mg⁻¹). To get the combined net GWP₁₀₀, the total CO₂ binding by the whole-wheat plant is credited (1,810,000 Mg y⁻¹). Fig. 5 shows a systems diagram that represents the GWP₁₀₀ flows from the different sources throughout the system life cycle per unit of total bioenergy produced (Table 8). This results in 57% reduction in GWP₁₀₀ from stand-alone wheat bioethanol and straw CHP systems compared to gasoline production and combustion system [14], natural gas-based heat generation system at 70% thermal efficiency [19] and soy meal production system [35] together.

Fig. 6 shows the percentage distribution of CPE, EP, AP and ARU for various subsystems included in the wheat bioethanol and straw CHP to grid system: whole-wheat cultivation, wheat bioethanol plant operation, straw CHP plant operation, transportation and construction. The hot spots in the system are wheat cultivation and bioethanol plant for CPE (48% and 50% respectively), as well as for ARU (52% and 46% respectively). EP and GWP₁₀₀ are distributed among the three subsystems: wheat cultivation (47% and 37% respectively), CHP plant (27% and 30% respectively) and bioethanol plant (26%, and 33% respectively). Wheat cultivation (91%) and bioethanol plant (8%) dominate the contribution to AP.

Table 8 – Annual products and bioenergy generated from the overall system (alternative 1).

Subsystem	Feedstock/Product	Flow rate (Gg)	Bioenergy (PJ)	Soy meal equivalent (Gg)
Cultivation	Wheat grain	1200	22.3	–
Bioethanol Plant	Ethanol	404	10.8	–
	DDGS	295	–	236
Cultivation	Wheat straw	361	5.27	–
Straw CHP Plant	Electricity	–	1.38	–
	Heat	–	0.737	–
Total bioenergy equivalent to gasoline and fossil CHP Systems			12.9	–

Results presented here are comparable with those reported in literature for similar systems. The GWP₁₀₀ (as CO₂-eq) value allocated to electricity (0.541 kg kWh⁻¹, without CO₂ balance consideration) from the CHP plant are comparable to those obtained from electricity generation from gasification of short rotation coppice willow chips of 0.482 kg kWh⁻¹ for GWP₁₀₀ with energy ratio of 19.3 [18]. The results of LCA of bioethanol and CHP production systems from wheat straw showed that the use of crop residues in a biorefinery reduces the GHG emissions by about 50% and fossil energy demand by more than 80% [16].

4. Integrated system GWP₁₀₀ and CPE saving analyses

The effect of the integration of the various bioenergy systems (straw- or DDGS-based CHP plant, heat production from DDGS and bioethanol plant) on the GWP₁₀₀ reduction and CPE saving from the production and usage of bioethanol in reference to gasoline was analysed. The calculation of the combined net GWP₁₀₀ and CPE was carried out following the substitution method taking the credits from the equivalent fossil-based energy and soy meal replacement by DDGS. The comparative reference systems for heat and electricity from straw are natural gas boiler for the generation of heat and grid

electricity (UK electricity mix), respectively. Table 9 summarises the results of GWP₁₀₀, CPE, bioenergy production and the corresponding savings for each case. Additionally, an integrated system (5) wherein a part of DDGS-based heat and straw-based CHP are used in the wheat bioethanol plant is considered.

Analysing the wheat grain production and bioethanol plant operation using the heat from the natural gas boiler and electricity from grid (1), the resulting GWP₁₀₀ comes from the cultivation of grain (economic allocation, Table 3), bioethanol plant operation and construction, raw materials transportation (Fig. 4), bioethanol transportation calculated assuming distribution within a radius of 120 km, ethanol combustion, and the corresponding CO₂ binding to wheat grain (Table 7). The credit from replacing 236,000 Mg y⁻¹ of soy meal equivalent is –171,000 Mg y⁻¹. The net GWP₁₀₀ of 422,000 Mg y⁻¹ corresponds to 39.0 g MJ⁻¹ (Table 9), thus achieving a reduction by 54%. This GWP₁₀₀ from overall wheat bioethanol and DDGS system is less than the impact allocated to cradle to bioethanol product utilisation route by economic values in Table 7, due to the account of credit from the replacement of soy meal by DDGS.

Nevertheless, both approaches (39% based on bioethanol allocation and 54% based on bioethanol and DDGS co-production and utilisation, respectively) demonstrate that a stand-alone UK wheat bioethanol subsystem may not meet

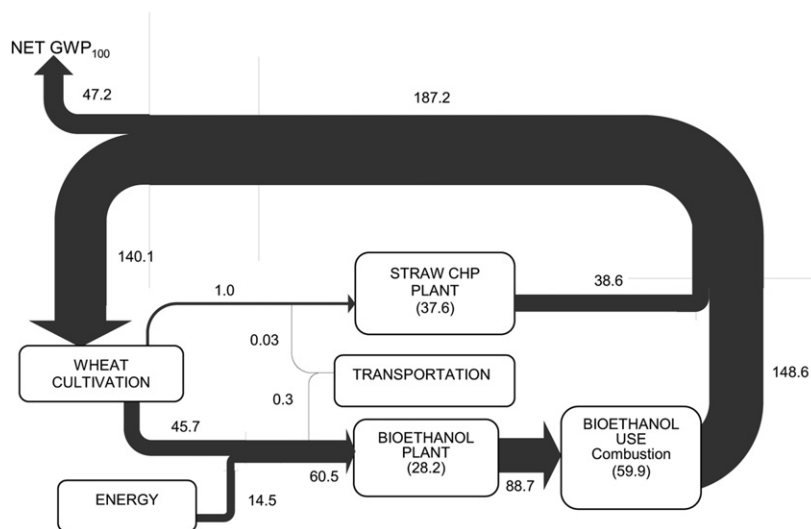


Fig. 5 – Life cycle GWP₁₀₀ (CO₂-eq), in g MJ⁻¹, of the production of bioenergy (as ethanol, heat and electricity) and DDGS in a whole-wheat-based system. Values for CHP and bioethanol plant include GWP₁₀₀ from other raw materials, process emissions and construction.

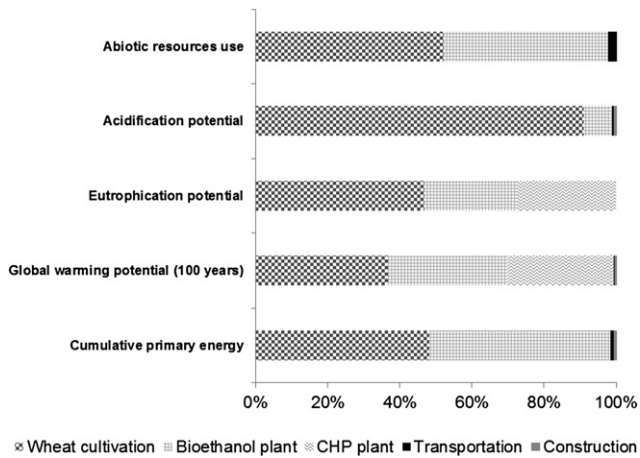


Fig. 6 – Environmental impact of wheat bioethanol and straw CHP to grid system.

the EU Renewable Energy Directive constraint on GHG emission reduction by >60% by 2020. Therefore, other alternatives to improve environmental performance of the bioethanol production need to be studied. In case of CPE, the saving is 56% with respect to the production of gasoline. The following cases make reference to the values from the wheat bioethanol plant as in base case (1).

For alternative number (2), the production of 2.95 PJ y^{-1} of heat from burning all the DDGS (LHV of 18.2 MJ kg^{-1} , carbon mass content of 45%) [37] is utilised within the bioethanol plant. The bioethanol plant heat requirement (as steam) from natural gas is completely replaced by the heat from DDGS and 0.95 PJ y^{-1} of excess heat is produced for the grid. Therefore, the CPE of 2.03 PJ y^{-1} and 1.36 PJ y^{-1} , respectively, are subtracted from the base case and the net CPE of the system is reduced to 3.20 PJ y^{-1} . The net bioenergy produced is now of 11.8 PJ y^{-1} and the overall effect is an increase in the energy ratio to 3.67. This gives savings of 77% in fossil CPE from the production of bioethanol with respect to the production of gasoline. However, the net GWP₁₀₀ (as CO₂-eq) is increased to $874,000 \text{ Mg y}^{-1}$ due to the addition of $487,000 \text{ Mg y}^{-1}$ from DDGS combustion, even after the credits from the replacement of $122,000 \text{ Mg y}^{-1}$ and excess heat of $83,300 \text{ Mg y}^{-1}$ (Table 9). No additional CO₂ binding is credited since DDGS comes from the processing of wheat grain (and the corresponding credit was already accounted in the base case (1)). Also, the electricity is supplied from the grid. As a result, the balance over case (2) indicates higher GWP₁₀₀ impact of 80.9 g MJ^{-1} bioethanol produced yielding a marginal saving by 4%.

An alternative 3, where the DDGS (moisture and ash mass contents of 8% and 3.9% respectively) is used as a raw material for the CHP plant and the energy generated is delivered to the bioethanol plant and the excess electricity is exported to grid, is considered. The DDGS conversion process provides

Table 9 – Summary of overall results on GWP₁₀₀ (CO₂-eq) in Mg y^{-1} , CPE in PJ y^{-1} and corresponding savings.

Alternative	(1)	(2)	(3)	(4)	(5)
<i>GWP₁₀₀ from different subsystems and combustion</i>					
Cultivation	591,000	591,000	591,000	604,000	604,000
Bioethanol plant	555,000	555,000	555,000	555,000	555,000
CO ₂ binding	–1,330,000	–1,330,000	–1,330,000	–1,810,000	–1,810,000
Ethanol combustion	774,000	774,000	774,000	774,000	774,000
DDGS combustion	–	487,000	–	–	208,000
CHP plant	–	–	488,000	487,000	487,000
Subtotal GWP₁₀₀	590,000	1,080,000	1,080,000	610,000	818,000
<i>CPE and GWP₁₀₀ credits</i>					
<i>From DDGS replacing soy meal</i>					
GWP ₁₀₀ credit	171,000	0	0	171,000	98,000
CPE credit	0.98	0	0	0.98	0.56
<i>From fossil-based energy replaced</i>					
Heat	–	2.95	0.78	0.74	2
GWP ₁₀₀ credit	–	206,000	48,100	45,100	122,000
CPE credit	–	3.39	0.79	0.75	2.03
Electricity	–	0	1.47	1.38	1.38
GWP ₁₀₀	–	0	273,000	256,000	256,000
CPE	–	0	4.73	4.44	4.44
Net GWP ₁₀₀ after credits	422,000	874,000	760,000	137,000	341,000
Net CPE after credits	5.62	3.20	1.09	0.47	–0.43
<i>Values from reference fuel (gasoline)</i>					
GWP ₁₀₀	914,000				
CPE	12.9				
<i>Final results</i>					
Net bioenergy	10.8	11.8	12.2	12.1	12.1
GWP ₁₀₀ (g MJ ^{–1})	39.02	80.91	70.37	12.63	31.55
GWP ₁₀₀ reduction	54%	4%	17%	85%	63%
E _{ratio}	1.92	3.67	11.10	27.62	–
CPE saving	56%	77%	92%	97%	103%

0.78 PJ y⁻¹ of heat and 1.47 PJ y⁻¹ of electricity. All the electricity requirements (0.12 PJ y⁻¹) by the bioethanol plant are thus completely replaced by the renewable electricity. 39% of the heat required by the bioethanol plant is also replaced. Thus, the corresponding credits can be subtracted from the impacts of the base case as before. Thus, after using the heat and required electricity within the bioethanol plant, the net bioenergy produced by the bioethanol (10.8 PJ y⁻¹) and DDGS CHP (1.4 PJ y⁻¹) system is 12.2 PJ y⁻¹. As in case (2), the net GWP₁₀₀ is increased from that of the base case due to the fact that CO₂ emissions are added to the system from the DDGS CHP plant and there is no credit for DDGS replacing soy meal. This system benefits from the production of renewable electricity and can achieve GWP₁₀₀ savings by 17% after credits. 93% of the CPE is replaced by an equivalent amount of bio-energy (bioethanol-DDGS-based CHP).

In alternative (4), the straw-based CHP is integrated with the bioethanol plant. The allocated GWP₁₀₀ to straw from the wheat cultivation system must be included into the base case GWP₁₀₀. Additionally, the CPE and the GWP₁₀₀ from the straw-based CHP plant operation and construction and straw transportation should be added. However, the integration of straw-based CHP with bioethanol plant can take advantage of additional CO₂ binding by the straw. Besides, DDGS is sold for animal feed, replacing soy meal and gaining the corresponding credits as in the base case (1). Similarly to case (3), the straw-based CHP plant replaces a part of the heat required by the bioethanol plant (37%) and there is excess electricity exported to grid. The resulting net GWP₁₀₀ reduction is 85%, fulfilling the EU Directive 60% emission reduction target. By taking all the credits, the CPE requirement by the system reduces by 97%. The net bioenergy is 12.1 PJ y⁻¹ (Table 9) from 172,370 ha of grade 3 land use (Table 3) providing land energy yield of 70 GJ ha⁻¹ y⁻¹.

Case 5 was explored by integrating the bioethanol plant with the straw-based CHP plant and DDGS combustion to supply the balance of heat (steam) required by the bioethanol plant. This case is a combination between cases 2 and 4. The integration is about supplying the entire heat requirement of 2.0 PJ y⁻¹ from the straw CHP plant (0.74 PJ y⁻¹) and from the DDGS heat (1.26 PJ y⁻¹) that completely replace the fossil-based heat (steam). The electricity requirement and the excess electricity generation are similar as in case 4. 126,000 Mg y⁻¹ of DDGS are required (assuming energy content as in case 2) to supply the balance of heat. Therefore, the system can still gain credits from 168,000 Mg y⁻¹ of DDGS replacing 135,000 Mg y⁻¹ soy meal, thus resulting in GWP₁₀₀ and CPE savings. The overall GHG emission reduction is 63% with respect to the use of gasoline. The CPE for the base case (1) is not only replaced by the production of bioenergy, but also additional energy in the form of excess electricity and bioethanol is saved. This system thus also achieves the EU Directive's 60% GHG emission reduction target.

In summary, the integration of wheat straw CHP and bioethanol plant proved to be an effective way to achieve the EU Directive GWP₁₀₀ reduction target, while saving fossil CPE. The complete replacement of heat (steam) and electricity by straw CHP and DDGS in alternative 5 is another option in which GWP₁₀₀ is lower but more fossil CPE can be saved. The incentives for the reduction of GWP₁₀₀ beyond the target and the capital costs involved in the two integrated systems would

finally determine the selection of one of these alternatives. The LCA approach presented took detailed account of CO₂ binding by wheat plant and the emissions from fermentation and combustion (ethanol, DDGS and/or straw). The saving results found for alternatives 4 and 5 are similar to those reported in Ref. [16].

5. Conclusions

A cradle-to-grave LCA of the UK whole-wheat-based bioethanol and straw-based CHP system has been performed considering the various IC including GWP₁₀₀ and CPE. It is demonstrated that the wheat cultivation, wheat bioethanol plant and straw CHP plant, if deployed in an integrated manner, can be more environmentally sustainable than the reference fossil-based system.

A transparent and comprehensive approach that included LCA of the UK whole-wheat cultivation, transportation and construction and operation of plants and utilisation of end products has been demonstrated. The analysis showed that the state-of-the-art bioethanol systems may not achieve the EU Directives' minimum GHG emission reduction target of 60%. Therefore, five integrated systems, wherein bioethanol energy requirements were met by lignocellulosic energy, were proposed. Cases 2 and 3, with DDGS used as a source of heat and CHP, respectively, improve the energy use of the system thereby saving CPE, but incur no emission reduction. The other two integration alternatives with bioethanol energy requirements met by straw CHP (alternative 4) and straw CHP and DDGS heat (alternative 5) respectively, achieve the EU Directive's target GHG reductions. The system in alternative 4 offers GWP₁₀₀ reduction by 85% and CPE savings by 97%, whilst the system in alternative 5 achieves the EU Directive's target GWP₁₀₀ reduction (63%) and CPE saving of more than 100%. The system assessed has also the advantage that no land use change is involved and impact on water is also negligible. A high yield of total bioenergy per ha must be attained implying an efficient use of land, a factor that is important considering that the land is a limiting resource. Concluding from various integration synergies within bioenergy systems and integrated energy system alternatives this study clearly demonstrates an urgent need for greater exploitation of lignocellulosic energy systems into biorefineries.

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Chapter 4

Integrated Jatropha-based biorefineries

4.1 Preamble

The biofuel industry is an expanding sector that is increasingly affecting agricultural markets, with currently 65% of EU vegetable oils production converted into biodiesel, while 50% of Brazilian sugarcane and about 40% of US corn production are used for bioethanol production (OECD/FAO, 2012). Increases in agricultural commodity prices have raised concerns over the utilisation of 1st generation feedstock (food crops such as corn, wheat, soybean, and rapeseed) between energy and food production. Biorefineries using alternative feedstocks (e.g. lignocellulosic materials, algae and non-food crops such as Jatropha, switchgrass and miscanthus) to produce sustainable biofuel and other products are being studied (Demirbas, 2009; Naik et al., 2010; Carriqui et al., 2011).

Jatropha curcas L. is a perennial plant producing an oil-rich seed that is usually not used for food purposes and can be grown in water- and nutrient-scarce lands (Achten et al., 2007; Carels, 2009). The Jatropha oil is useful to produce transportation fuels such as biodiesel, synthetic/green diesel or jet fuel (Kumar et al., 2008). Native to Mexico and other Latin-American countries, Jatropha has raised promising expectations for sustainable production of biofuels, energy and other products and as a contributor for rural development in tropical regions such as India, China, West Africa and Malaysia (Achten et al., 2007). Despite the promises of Jatropha, agronomic issues regarding land use together with fertiliser and water requirements for increasing seed yield call for detailed inspection of the sustainability of Jatropha-based biorefinery systems. Designs for future deployment should aim to reduce the impacts and enhance the economic benefits on a life cycle basis.

As shown in the previous chapter for wheat biorefineries, process integration strategies are effective for integrated and efficient design of biorefinery platforms. The whole Jatropha fruit can be utilised integrating gasification, heterogeneous chemical conversion, anaerobic digestion and CHP generation processes to increase overall resource efficiency along with life cycle environmental impact reductions leading to more sustainable process designs.

4.2 Discussion of publication 3

Biorefineries fully exploiting Jatropha fruit are investigated in the paper presented in this chapter. The paper is based on the work presented in the 1st Iberoamerican Congress on Biorefineries (Martinez-Hernandez et al., 2012). The paper has been invited and submitted for the special issue in the Journal of Biomass Conversion and Biorefinery by Springer.

By converting Jatropha fruit residues (shells, husks) and processing co-products (seed cake, glycerol) into biofuels and electricity, additional energy, economic and environmental burdens can be avoided. Two alternative systems for the production of biodiesel and green diesel have been studied. The conversion processes using the by-product streams to supply utility and raw material are integrated around the biofuel production processes. The benefits from the integrated systems are evaluated with respect to the standalone plants and a fossil-based reference system. In the standalone plants, biofuels are produced using utility and auxiliary raw materials from fossil resources.

In the biodiesel system, transesterification of the oil using heterogeneous catalyst is carried out, while the husk is gasified into syngas and further converted into heat and power and methanol production in integrated biomass gasification and combined cycle system (IBGCC-MeOH). The alternatives for glycerol utilisation are as a chemical or as a substrate in anaerobic digestion. The green diesel system comprises hydrogenation of the oil while the husk is gasified into hydrogen-rich syngas production. Part of the syngas is used to supply hydrogen for the green diesel process and the rest is converted into heat and power, thus the system is named IBGCC-H₂. In the more advanced biorefinery schemes, the shells are converted into

biogas using anaerobic digestion, while the alternative uses for cake include animal feed and substrate in anaerobic digestion. The biorefinery is evaluated in the context of a Mexican plantation. Data on the current agricultural practices were communicated by Martinez-Herrera (2011). The cultivation of non-toxic *Jatropha* seed species native to Mexico allows the use of the oil extraction cake as animal feed (Rivera-Lorca, 1997; Martinez-Herrera, 2006).

A cradle-to-grave life cycle energy and global warming potential impact assessment has been applied to evaluate the systems' sustainability with respect to the reference systems. The modelling framework comprises *Jatropha* yield models in terms of cultivation and seed conditioning parameters and process simulations in Aspen Plus[®]. In both integrated diesel production systems, energy and global warming potential savings were twice that of the standalone system and above 100% with reference to a fossil-based system producing the same amount of output energy. Most of the benefits come from the conversion of seed husk into heat, power and methanol to supply to the biodiesel production, and heat, power and hydrogen to supply to the green diesel production processes. Additional savings are generated from the anaerobic digestion of fruit shell, cake and glycerol, although seed cake provides more credits when sold as animal feed or as fuel. Furthermore, taking the energy content of the whole fruit as basis, the energy efficiency of the conversion processes are higher in the best integrated biodiesel (14% higher) and green diesel (16% higher) systems fully exploiting *Jatropha* fruit than in the corresponding stand alone processes which convert only the *Jatropha* oil fraction.

The paper demonstrates that coupling the energy and raw material generation processes, utilising lignocellulosic residues, with the biofuel production processes improves the process performance from both energetic and environmental impact points of view. This reinforces the prominent role of process integration tools in future biorefinery deployments. The study also showed that energy resource depletion and global warming potential assessment alone was not enough to differentiate between the two biofuel alternatives being explored. However, due to its readiness for blending with petro-diesel at higher proportions, green diesel could be favoured from technical and infrastructural feasibility points of view (Huber, 2007; Huo, 2008).

Publication 3: Martinez-Hernandez, E., Martinez-Herrera, J., Campbell, G.M., Sadhukhan, J., 2013. *Process integration, energy and GHG emission analyses of Jatropha biorefinery systems*. Submitted to Biomass Conversion and Biorefinery.

**Process integration, energy and GHG emission analyses of Jatropha
biorefinery systems**

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ABSTRACT

Driven by the need to develop a wide variety of products that are environmentally feasible, biorefineries need to emerge as highly integrated facilities. This becomes effective when overall mass and energy integration through a centralised utility system design is undertaken. An approach combining process integration, energy and greenhouse gas (GHG) emission analyses is shown in this paper for Jatropha biorefinery design, primarily producing biodiesel using oil-based heterogeneously catalysed transesterification or green diesel using hydrotreatment. These processes are coupled with a husk-based gasification combined cycle co-producing heat and power with methanol in the biodiesel case or hydrogen in the green diesel case. This paper entails conversion of Jatropha by-products, fruit shell, cake, seed husk and/or glycerol in various processing routes such as combustion, gasification and anaerobic digestion, along with heat recovery within biodiesel or green diesel production and biorefinery total site utility network design. The biorefinery systems wherein cake supplies heat for oil extraction and seed drying while fruit shells and glycerol provide power generation via anaerobic digestion into biogas, achieve energy efficiency of 53% in the biodiesel system and 57% in the green diesel system based on high

heating values. Both systems exhibit a land to energy yield of 83 GJ ha⁻¹ and the GHG emissions, as global warming potential (CO₂-eq.), of the net bioenergy produced was 29 g MJ⁻¹ before accounting credits from displacement of fossil-based energy by excess bioenergy exported from the biorefineries.

Keywords: biodiesel, green diesel, biorefinery, utility system design, LCA, process integration.

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1. Introduction

Jatropha curcas as a low carbon feedstock for the production of biofuels has been explored in recent years in tropical countries such as India, China, Malaysia and Mexico, with about 1900 km² of plantations globally in 2008 and an expected growth to 130 000 km² by 2015 [1]. In order to establish *Jatropha curcas* as a competitive energy crop, every component of the whole fruit must extensively be extracted into added value productions within highly integrated biorefinery facilities. Whole *Jatropha* fruit components include fruit shells, seed husks, oil and cake after oil extraction from the kernel, presented along with compositions and energy values in **Table 1**. *Jatropha* oil has been extensively investigated for biodiesel production using homogeneous and heterogeneous catalysis [3], [4]. Heterogeneous catalysts (e.g. MgO, CaO, zeolites) facilitate separation of products and provide greater flexibility to free fatty acid content in oil [3]–[6]. An alternative to biodiesel is green diesel, which is produced alongside a propane fuel mixture as co-product, using hydrotreatment of vegetable oils [7]. This process has the advantage of the biofuel products being readily adaptable to current infrastructure [7].

50 **Table 1**

51 Conversion of whole *Jatropha* fruit into energy commodities might have up to three
52 times energy output than *Jatropha* oil to biodiesel production alone [8]. The
53 extraction cake can be used as a valuable source of protein and potential replacement
54 of soy meal for animal feed [9]–[14]. An alternative use of *Jatropha* cake is as an
55 organic fertiliser [12], [14], [15]. Cake and fruit shells are a good substrate for
56 anaerobic digestion into biogas [16]–[18]. Glycerol has also been studied as a
57 potential feedstock for biogas generation [19], [20]. *Jatropha* seed husk has been
58 explored as an attractive fuel for gasification and pyrolysis [8], [21], [22]. These
59 thermochemical processes can produce syngas or bio-oil for the generation of liquid
60 fuels, chemicals (e.g. methanol, hydrogen), heat and power from residues [23]–[29].
61 With systematic selection and process integration of co-production routes, fossil
62 energy use and global warming impact of biorefineries can be reduced [25]–[29].
63 Life cycle assessment (LCA) is an effective tool for analysing material and energy
64 inventories and environmental impacts throughout a product or process life cycle
65 [30]–[35]. LCA studies of *Jatropha*-based bioenergy systems have revealed
66 reductions in greenhouse gas (GHG) emissions in the range of 55%–90% with
67 savings in cumulative fossil primary energy (CPE) of more than 70%, in respect to a
68 reference fossil-based system [3], [32]–[35]. Although these studies considered
69 utilisation of various *Jatropha* fruit fractions and various conversion routes, potential
70 benefits from process integration opportunities have not been explored.
71 Starting with an effort to improve energy efficiency of process industries in 1970s,
72 the process integration tools [36]–[41] have been widely applied with valuable
73 contributions in the field of biorefineries such as process synthesis [39], [40], heat
74 and mass integration [23]–[25], pollution and GHG emission control [41],

75 optimisation of process and supply chain [42], and of energy and material efficiency
76 for reduced energy consumption [43]. Built upon the basic principles of
77 environmentally friendly process design with the most efficient use of raw materials
78 and energy, this work proposes an effective framework combining process
79 integration tools and LCA approach for more resource efficient and sustainable
80 biorefinery design. It is a matter of urgency to investigate systematic process
81 integration synergies and compare the energy and global warming impact from
82 greenhouse gas emissions between biorefinery integration alternatives. This paper
83 shows comparison between environmental sustainability and optimal process design
84 analyses between green diesel and biodiesel productions from integrated Jatropha
85 biorefinery systems in which the required electrical and thermal energy and hydrogen
86 or methanol are generated from Jatropha residues.

87 **2. Methodology**

88 **2.1 Goal and system definition**

89 The objective of this work is to produce integrated biorefinery schemes from
90 Jatropha fruit for the production of biofuels, power and co-products and assess the
91 environmental sustainability of such schemes in terms of GHG and cumulative
92 primary energy using life cycle analysis. On the basis of such assessment, the most
93 sustainable is recommended for future deployment. The energy efficiency and the
94 savings in respect to an equivalent fossil-based system are also assessed.

95 **Fig. 1** presents an overview of the system considered in this study. Two alternative
96 biofuel production systems are studied: biodiesel and green diesel. The base case
97 comprises the standalone biofuel plants wherein the oil is the only Jatropha fruit
98 fraction, converted into either biodiesel and glycerol or green diesel and a propane
99 fuel mix, with the oil extraction cake as a by-product in both cases. In these stand

100 alone systems, any utility requirements, after internal process integration, are
101 supplied from fossil sources.

102 In the ‘integrated biodiesel or green diesel systems’, the husk is gasified into syngas
103 which is used to supply combined heat and power (CHP), along with either methanol
104 for biodiesel or hydrogen for green diesel productions. The excess power is exported
105 to the electricity grid. As shown in **Fig. 1**, five alternatives for the use of fruit shells,
106 extraction cake and glycerol within the integrated systems are proposed for the whole
107 Jatropha utilisation to improve conversion efficiency:

108 **1)** Cake is used as fuel to supply heat for oil extraction (wherein natural gas is
109 substituted) and seed drying (wherein diesel is substituted).

110 **2)** Fruit shells are used as fuel to provide heat for oil extraction and seed drying.
111 Cake is used as fertiliser replacing part of the inorganic fertilisers currently used.

112 **3)** The same as alternative 2, but cake is sold as animal feed. Soy meal is replaced by
113 the cake.

114 **4)** Cake and fruit shells (and glycerol in the biodiesel case) are used in anaerobic
115 digestion. The biogas produced is converted into electricity.

116 **5)** Cake supplying heat for oil extraction and seed drying as in alternative 1. The fruit
117 shells and glycerol in the biodiesel system are used as in alternative 4.

118 **Fig. 1** Overview of the integrated Jatropha biorefinery systems for the production of
119 biodiesel and green diesel with utilities and auxiliary raw materials generated from
120 Jatropha by-products. Numbers 1–5 indicate in which alternative the options for by-
121 product utilisation are selected. Mass flow rate in Gg y⁻¹, Heat and power in PJ y⁻¹.

122 IBGCC: Integrated biomass gasification and combined cycle

123 Substitution approach by taking credits from co-products has been used. GHG
124 emissions have been characterised by their global warming potential (GWP) impact

as CO₂-eq. The biorefinery is assumed to be located within the radius of a plantation in Mexico. Transportation distance for fruit shells, seeds and cake is equal to the radius of the plantation land assuming a circular shape. The transportation of auxiliary raw materials and biorefinery products are assumed to be 100 km (average distance measured using Google[®] maps tool). The CPE and GWP factors are based on road transportation using 100% fossil-based diesel [45]. The embodied CPE and GWP impact of the various fuels and raw materials are extracted from various sources [45]–[49] and are presented in **Table 2**. The fossil-based cumulative primary energy and environmental impact data for power are deduced from [46] and the Mexican national electricity mix data (natural gas = 51.8%, fuel oil = 16.7%, coal = 12.4%, diesel = 0.5%, renewable = 14.1% and nuclear = 4.5% by energy) [50].

Table 2

2.2 Modelling approaches for inventories

The systematic analysis comprises detailed modelling for the *Jatropha* cultivation, including seed yield modelling, and seed drying and conditioning using spreadsheet calculations. Spreadsheet based models were also used for seed processing, anaerobic digestion and biogas conversion to power. Process simulations using Aspen Plus[®] were developed to estimate the inventories from *Jatropha* oil conversion to biodiesel or green diesel and from husk conversion to heat, power and hydrogen or methanol. The basis for the mass and energy balances is the production of 100 Gg y⁻¹ of biodiesel from 104.7 Gg y⁻¹ of *Jatropha* oil. The functional unit for green diesel system is 93.4 Gg y⁻¹ of green diesel from the same amount of *Jatropha* oil as in the biodiesel system. These amounts also set the mass and energy flow rates of all other *Jatropha* fractions based on the yields provided in **Table 1**. The results from *Jatropha* cultivation and seed processing are common to all the alternatives studied

(standalone and integrated systems). Raw material and energy inventory data are then extracted for overall system GWP and CPE assessments. The various modelling approaches required by the main subsystems in the overall Jatropha system are presented as follows.

2.2.1. Jatropha yield model

An empirical model correlating seed yield to average annual rainfall (AAR) and nitrogen fertilisation rate (N) is shown using reported seed yield from field experiences around the world presented in **Table 3**.

Table 3

The annual seed yields at maturity Y_{mat} (in kg ha^{-1} ; 1 ha= 0.01 km^2) under natural conditions, i.e. without nutrient or water management, in **Table 3** were determined from the Chapman–Richards correlation shown in **Eq. 1** [51]. Y_{age} in (kg ha^{-1}) is the yield at a given plant age (A) and the model coefficients for Jatropha are $b=0.852$ and $c=3.466$ [51].

$$Y_{age} = Y_{mat} (1 - e^{-bA})^c \quad (1)$$

Assuming that the yield values in **Table 3** are for Jatropha grown under rain fed conditions, the calculated values of Y_{mat} are correlated to AAR. A third order polynomial function can be applied to fit the data in **Table 3** as shown in **Eq. 2**

$$Y_{mat}^{AAR} = a_1 AAR^3 + a_2 AAR^2 - a_3 AAR \quad (2)$$

Y_{mat}^{AAR} is the annual seed yield at maturity (in kg ha^{-1}) and a given AAR (in mm).

The total annual seed yield at maturity considering nitrogen fertilisation, Y_{mat}^N (in kg ha^{-1}) is correlated to its base value at annual average rainfall of a location (Y_{mat}^{AAR} in kg ha^{-1}) and the nitrogen fertilisation rate, N (kg ha^{-1}), shown in **Eq. 3**, based on

conditions [52], similar to a plantation located in Michoacan, Mexico. **Table 4** shows the values of the parametric coefficients and constants in Eq. 2 and Eq. 3.

$$Y_{mat}^N = Y_{mat}^{AAR} + b_1(1 - e^{-b_2N}) - b_3N \quad (3)$$

The Jatropha field measurement from the plantation in Michoacan, Mexico was used as a test case to validate the model. For this plantation, a nitrogen fertilisation rate of 162 kg ha⁻¹ is applied and the AAR of the location is 900 mm (Personal communication from one of the authors, Dr. Jorge Martinez-Herrera). Doing a backward calculation from **Eq. 3** to **Eq. 1**, the estimated seed yield in the fifth year was $Y_{age} = 4010 \text{ kg ha}^{-1}$. The observed annual seed yield is about $Y_{age} = 4000 \text{ kg ha}^{-1}$ in the fifth year. Comparing the predicted and observed value of Y_{age} , the error was 0.25%.

2.2.2 Jatropha cultivation

The plantation in Michoacan, Mexico used for model validation above was taken as a basis for CPE and GWP assessment of Jatropha cultivation. The different stages in a Jatropha cultivation system are shown in **Fig. 2**. The estimated seed yield at maturity of 4213 kg ha⁻¹, from the yield model, was employed in LCA calculations. A lifespan of 24 years was considered including four years to allow plants to reach maturity (establishment stage). The inventories in the Jatropha cultivation are summarised in **Table 5**.

Fig. 2 The Jatropha cultivation system producing seeds conditioned in field

Table 5

The annual seed yield at maturity contains 114.3 GJ ha⁻¹ energy and the corresponding fruit shells contains 32.7 GJ ha⁻¹ of energy (based on the heating values given in **Table 1**). The land use requirement is about 64385 ha (644 km²). The calculated radius is 14.3 km for the Jatropha seed production of 271.2 Gg y⁻¹

198 required for the extraction of 104.7 Gg y^{-1} of oil which is converted into either
199 biodiesel or green diesel.

200 **2.2.3. Seed processing**

201 Dried seeds transported to the biorefinery plant are first dehusked into kernel and
202 husks. Kernels are sent to an integrated solvent oil extraction process producing high
203 quality oil and dried cake. In the stand alone systems, the seed husks are not
204 considered as a co-product. Inventories consist of electricity, heat and make-up
205 hexane [53].

206 **2.2.4 Biodiesel plant**

207 Inventories of a biodiesel plant were determined by simulating the plant in Aspen
208 Plus in **Fig. 3** based on process specifications in **Table 6**. Oil was modelled as a
209 mixture of tryglycerides (TG) made up of four major components (triolein,
210 tripalmitin, trilinolein and tristearin) and average free fatty acids (FFA) content as
211 oleic acid. Properties of these components and the corresponding fatty acid methyl
212 esters (FAME) were predicted using the UNIFAC-Dortmund physical property
213 model [54].

214 **Fig. 3** Simulation of biodiesel production plant by heterogeneous transesterification
215 of Jatropha oil

216 **Table 6**

217 A heterogeneously catalysed transesterification process was considered for FAME
218 production using calcium oxide catalyst at 70°C and a methanol-to-oil molar ratio of
219 9 [4]. Since no kinetic data is available for this catalyst and only the yield is
220 available, the transesterification reactor (TREACT) was simulated using the
221 stoichiometric reactor model in Aspen Plus with the conversions specified in **Table**
222 **6**. Excess methanol was recovered by vacuum distillation and recycled. Distillation

223 facilitated downstream separation between glycerol and methyl ester phases in a
224 decanter. Thus, water washing and neutralisation reactors required in a typical
225 homogeneously catalysed process were avoided.

226 Following a heat integration strategy and using hot and cold composite curve
227 analyses [36], the reaction mix stream (REACMIX) was preheated (from 25 °C to 70
228 °C and duty of RMIXHTR in **Fig. 3**) by the bottom stream of the methanol recovery
229 column (MRECBOT from 167 °C to 135 °C), before entering the transesterification
230 reactor (TREACT at 70 °C). The crude biodiesel stream (CRUDEFAME at 25 °C)
231 fed to the recovery column was also preheated to 301 °C in PREH1 by the distillate
232 biodiesel stream (DISTBDSL, at 317 °C cooled to 35 °C) thus reducing reboiler
233 duty. After these heat recoveries, 0.11 PJ y⁻¹ of medium pressure (MP) steam and
234 0.04 PJ y⁻¹ of high pressure (HP) steam were required.

235 **2.2.5 Green diesel plant**

236 Jatropha oil conversion to renewable or green diesel was simulated based on NREL
237 (US) studies, which were validated against pilot plant results [7]. **Fig. 4** shows the
238 flowsheet and material balance for the green diesel process. The same amount of oil
239 feed (104.7 Gg y⁻¹), composition and properties as in the biodiesel plant were input
240 to the simulation. A reactor yield model was used in Aspen Plus for the
241 hydrotreatment reactor (H2TRECTR). The yield fractions and the complete set of
242 specifications for the simulation are summarised in **Table 7**. Green diesel was
243 modelled as C₁₈H₃₈. 0.027 kg of fresh H₂ and 0.028 kg of LP steam (0.5 MPa) were
244 required for the processing of 1 kg of Jatropha oil. 93.4 Gg y⁻¹ of green diesel was
245 separated through flashing and stripping with LP steam. Thus, 1.121 kg of Jatropha
246 oil is required to produce 1 kg of green diesel. 3.4 Gg y⁻¹ of propane fuel mix is co-
247 produced. The process incurred a direct CO₂ emission per unit of mass of green

248 diesel equal to 0.12 kg kg^{-1} . Hydrogen from natural gas steam reforming was
249 supplied to the plant.

250 **Fig. 4** Simulation of green diesel production plant by hydrotreatment of Jatropha oil

251 **Table 7**

252 **2.2.6 Husk gasification systems**

253 The proposed IBGCC scheme converts seed husk in an allothermal gasifier into a gas
254 rich in hydrogen and CO [24]. The gasifier comprises of a fluidised bed steam
255 gasification reactor and a char combustor for indirect heating of the steam
256 gasification reactor. After gas clean-up, the syngas was converted into methanol and
257 CHP [23], [24] to supply the biodiesel process. Alternatively, hydrogen is separated
258 from part of the syngas to supply the green diesel process with the other part of
259 syngas also converted into CHP. Jatropha seed husk, with an elemental analysis in

260 **Table 1** and a proximate analysis (in mass fraction) made up of moisture (10.75%),
261 volatile matter (63.40%), fixed carbon (22.30%) and ash (3.54%), formed a basis for
262 the estimation of the primary pyrolysis product yields as in [24]. The simulation was
263 carried out for 91.4 Gg y^{-1} of seed husk resulting from the seeds processed into oil.
264 The simulation flowsheets and mass balances of the husk IBGCC plants for methanol
265 (IBGCC-MeOH) or hydrogen (IBGCC- H_2) production are shown in **Fig. 5** and **Fig.**
266 **6**, respectively. The equipment specifications and how each process unit was
267 modelled in Aspen Plus are shown in **Table 8**. Equilibrium reactors have been
268 adapted for the simulation of water-gas shift reactor (WGSR) and methanol reactor
269 (MEOHREAC) while Gibbs reactors were used to simulate the gasifier (STGASIFY)
270 and combustor (COMBUSTR). Gas clean-up unit (GCLEANUP) and pressure swing
271 absorption unit for hydrogen separation (PSA) have been simulated assuming typical
272 split fractions (**Table 8**). Other separators were simulated using rigorous flash model

as specified in **Table 8**. Due to the lack of experimental or pilot plant data, these models and assumptions are commonly used and have been validated in literature for estimation purposes [23], [24]. A water-gas shift reactor was coupled to the gasifier to adjust the required syngas composition for methanol or hydrogen co-production. From a sensitivity study, a steam to biomass mass ratio of 0.34 was required in the case of methanol co-production and of 0.7 in the case of hydrogen co-production. No additional steam was required for the WGSR.

Fig. 5 Simulation of Jatropha seed husk IBGCC-MeOH plant

Fig. 6 Simulation of Jatropha seed husk IBGCC-H₂ plant

The gas after removal of H₂S and CO₂ was further conditioned to a stoichiometric number ($SN = 2.06$) suitable for methanol [23] as well as hydrogen-rich syngas production (via PSA process). Based on the process specifications in **Table 8**, the mass and energy balances around the key reaction processes, steam gasification (STGASIFY), char combustor (COMBUSTR), WGSR and methanol synthesis reactor (MEOHREAC) in **Fig. 5** and **Fig. 6**, were established [24], [24]. The clean syngas was purified in a PSA unit for hydrogen production. The remaining syngas (SYNGFUEL), after meeting the demands for methanol or hydrogen as well as the off-gas streams from MEOHREC (**Fig. 5**) or PSA (**Fig. 6**) processes, was sent as fuels to COMBUSTR. The off-gas from PSA was compressed in OFFGCOMP before feeding to COMBUSTR (**Fig. 6**). A part of the combustion heat was used in the gasifier and the rest was recovered into CHP generation via steam as described below.

Table 8

2.2.7 Anaerobic digestion and biogas power

297 Anaerobic digestion of Jatropha by-products and residues were modelled as a linear
298 input-output correlation based on reported biogas yields from literature in
299 spreadsheets. This is due to the lack of more detailed data for the modelling of the
300 anaerobic digestion for the particular combination of substrates studied in this paper.
301 The biogas productions (with CH₄ volume fraction of 70%) of 0.546 m³ from 1 kg of
302 fruit shell [17] and 0.347 m³ from 1 kg of dry cake [16] were taken as the basis. In
303 the integrated biodiesel system, 1 kg of glycerol was also digested into 0.306 m³ of
304 CH₄, volume fraction of which in the biogas is 75% [19]. The alternative system 4
305 involves anaerobic digestion (AD) of Jatropha cake, fruit shells and glycerol and
306 power production from the resulting biogas in a combined cycle. About 96 Gg y⁻¹ of
307 biogas can be produced by digesting the three substrates in the integrated biodiesel
308 system alternative 4, resulting in 1.21 PJ y⁻¹ of power generation. After meeting heat
309 and power requirements by the digester [20], the net exported power was 1.10 PJ y⁻¹.
310 In the integrated green diesel biorefinery system alternative 4, the cake and shells
311 were the substrates in anaerobic digestion with net exported power of 1.04 PJ y⁻¹.

312 **3. Results and discussion – Jatropha cultivation and stand alone systems**

313 **3.1 Jatropha cultivation**

314 **Fig. 7** shows the resulting CPE and GWP impacts from Jatropha cultivation. The
315 main contribution to the CPE impacts is from the manufacture of fertilisers, seed
316 conditioning and storage. The GWP impact is mainly contributed by the field
317 emissions due to nitrogen fertilisation, manufacture of fertilisers and seed
318 conditioning. The cultivation system requires 0.14 PJ y⁻¹ diesel, 0.25 PJ y⁻¹ heat and
319 1970 GJ y⁻¹ power. The CPE and GWP (as CO₂-eq) impact allocations to seeds are
320 5.4 MJ kg⁻¹ and 0.63 kg kg⁻¹, respectively.

321 **Fig. 7** Results of CPE and GWP impacts from Jatropha cultivation

322 3.2 Stand-alone biodiesel and green diesel plants (base cases)

323 The co-products from stand-alone biodiesel and green diesel plants are the extracted
324 cake, glycerol (in biodiesel plant) and propane fuel mix (PFM, in green diesel plant).

325 The fossil-based equivalent products are fuel oil for glycerol and liquefied petroleum
326 gas (LPG) for PFM. In the case of cake being used for animal feed, 1 kg of cake
327 could replace 1.4 kg of soy meal according to protein content comparisons [11]. The
328 inventory and impact analyses for the various processes are discussed as follows.

329 0.40 PJ y^{-1} of heat and 0.06 PJ y^{-1} of power were required for seed processing [53].

330 The CPE from seed processing (a total of 0.78 PJ y^{-1}) was contributed by hexane by
331 5.2%, natural gas for heat production (at 70% efficiency) by 75.1% and power by
332 19.7%. The GWP (a total of 46.7 Gg y^{-1}) contributions from these sources were 2%,
333 75.8% and 22.1% respectively.

334 The cradle-to-gate LCA results for the biodiesel standalone production system are
335 presented in **Table 9**. The GWP impact (as $\text{CO}_2\text{-eq}$) from biodiesel production was
336 43.3 g MJ^{-1} leading to 42% saving in respect to diesel. The CPE per unit of energy in
337 biodiesel was 0.51 MJ MJ^{-1} , leading to 54% saving in respect to diesel. The
338 operating energy efficiency, $E_{op} = \text{Energy output in all products} / (\text{Energy content in}$
339 $\text{all feedstock} + \text{direct energy consumption})$, is 91%.

340 **Table 9**

341 The LCA results for the cradle-to-gate green diesel standalone production system are
342 presented in **Table 9**. A GWP (as $\text{CO}_2\text{-eq}$) of 39.9 g MJ^{-1} was estimated for green
343 diesel. This result is comparable to the value of 45.5 g MJ^{-1} for green diesel from
344 soybean oil reported in [7]. The resulting GWP saving was 46%. The CPE per unit of
345 energy in green diesel was 0.56 MJ MJ^{-1} , resulting in a saving of 52% with respect to
346 diesel. About 85% of the CPE and GWP impacts resulted from the imported

hydrogen. Contribution from power generation to CPE and GWP impacts is 10.7% and 11.1%. The contribution from MP steam production is 3.2% to CPE and 2.9% to GWP. The rest is contributed by LP steam production. Energy input is 0.02 PJ y⁻¹ as heat, 0.03 PJ y⁻¹ as power, 0.40 PJ y⁻¹ as hydrogen (HHV=141.8 MJ kg⁻¹) and 4.15 PJ y⁻¹ as oil (HHV=39.63 MJ kg⁻¹). The energy contained in green diesel (HHV=45.80 MJ kg⁻¹) is 4.28 PJ y⁻¹ and in PFM (HHV= 46.26 MJ kg⁻¹) is 0.16 PJ y⁻¹. Thus, the operating energy efficiency of Jatropha utilisation in the process is E_{op} = 96%.

However, the overall system includes the energy required in cultivation (0.39 PJ y⁻¹ in Section 4.1), seed processing (0.47 PJ y⁻¹ in Section 4.2.1) as well as the energy wasted in seed husk (1.82 PJ y⁻¹), fruit shells (2.11 PJ y⁻¹) and extraction cake (1.37 PJ y⁻¹). By considering all this energy inputs, the energy efficiency of the green diesel standalone plant is just $E_{op} = 4.44/10.76 = 41\%$. Similar calculations show that the energy efficiency of the biodiesel standalone plant is 39%. These results indicate a potential for improving the efficiency of Jatropha conversion for energy production in both biofuel production systems.

There is potential for improving CPE and GWP savings by replacement of the utilities and hydrogen derived from fossil resources, by those derived from biomass feedstocks such as the Jatropha residues and by-products. These biorefinery integration opportunities are shown in the following sections as options for environmental sustainability improvement.

4. Results and discussion – integrated biorefinery systems

4.1 Process integration for GWP and CPE reduction

A systematic heat integration methodology and CHP network design for the recovery of maximum heat and power as a product enhancing the energy efficiency of an

overall biorefinery system was shown in [23], [24]. The design procedure encompasses the pinch analysis for process to process heat recovery network design. Any excess heat is extracted into steam generation. The superheated steam generation must be maximised at the highest pressure level, such as very high pressure (VHP) steam. Thereafter, lower pressure superheated steam can be generated if heat is available at lower pressure level. To ensure feasible heat integration, a minimum approach temperature between hot and cold streams must be maintained to avoid temperature crossing. A minimum approach temperature difference of 20 °C for heat recovery into steam and 10 °C for heat exchange between process streams can be initially used from typical values reported in the literature [23], [36]. These values can be later optimised by considering economic costs [36].

The CHP networks of the proposed schemes for Jatropha-based integrated biorefineries were designed to meet the heat, and methanol or hydrogen demands of the respective biofuel plants using simulations in Aspen Plus[®]. The composite curves used to determine steam generation potential in the main heat recovery exchangers (HRSG1, HRSG2 and SYNGCOOL) are presented in **Fig. A.1** of Appendix A. The exothermic heat of reaction from WGSR and MEOHREAC can be extracted into MP steam generation on the shell side of the reactor [23]. The excess heat of combustion in COMBUSTR (i.e. after meeting heat demand for gasifier) is extracted into very high pressure steam (VHP). Any excess heat energy recovered via steam generation is converted into power generation displacing the grid electricity. The amounts of steam and power were determined from simulation in Aspen Plus[®]. The simulation flowsheets for the designed CHP networks are shown in **Fig. A.2** and **Fig. A.3** of

Appendix A. The steam and power balances in the CHP networks are shown in **Fig. 8** and described as follows:

Fig. 8 CHP network of husk processing into a) IBGCC-MeOH and b) IBGCC-H₂

- The steam levels were set by the temperature levels of the various processes. Very high pressure (VHP) steam at 100 MPa and 650 °C, medium pressure (MP) steam at 1.5 MPa and low pressure (LP) steam at 0.5 MPa were generated in both IBGCC-H₂ and IBGCC-MeOH systems.

- High pressure (HP) steam was generated at 3 MPa and 650 °C by recovering heat from the gasifier product gas in a high recovery steam generator (HRSG1). In IBGCC-MeOH, the surplus HP steam, after meeting the gasifier steam requirement, was used in back-pressure steam turbine ST3. In IBGCC-H₂ plant, all the steam produced in HRSG1 was used in the gasifier.

- In both IBGCC systems, the heat in the flue gas from the combustor (COMBUSTR, at 1200 °C) was recovered into VHP steam generation in a high recovery steam generator (HRSG2). The same flue gas was further expanded in a turbo-expander (TEXP) to generate power for the air compressor (AIRCOMPR in **Fig. 5** and **Fig. 6**). Thus surplus power was generated. In the integrated biodiesel system, the VHP steam generated in HRSG2 was first used to fulfil the heat requirement by the reboiler in the biodiesel recovery column before generating power from the back-pressure steam turbine ST1 (**Fig. 8**).

- The surplus exothermic heat of reaction of the combustor (COMBUSTR), after meeting the heat requirements of the gasifier, was also recovered into VHP steam generation. In the IBGCC-H₂, all the VHP steam generated from COMBUSTR and HRSG2 was expanded through the back-pressure steam turbine (ST1) to an

420 outlet pressure of 0.5 MPa for power generation since there was no demand for VHP
421 steam in the green diesel plant.

422 • Exothermic heat from WGSR and MEOHREAC (in IBGCC-MeOH plant)
423 and the excess heat in SYNGCOOL were suitable for MP steam generation. In the
424 green diesel and IBGCC-H₂ integrated system, part of the MP steam generated was
425 used in the oil preheater (RMIXHTR, **Fig. 4**) and the excess was utilised for power
426 generation in back-pressure steam turbine (ST2). In the biodiesel and IBGCC-MeOH
427 integrated system, all the MP steam generated was used to fulfil the heat demands by
428 the biodiesel plant.

429 • LP steam generated after expansion of steam at higher levels was used to
430 meet heat demands by the gas clean up and biodiesel or green diesel plants. Surplus
431 LP steam was passed through condensing steam turbine for power generation. The
432 condensate was returned as boiler feed water.

433 • The waste heat available in the syngas stream after heat recovery as MP
434 steam in SYNGCOOL (in both IBGCC-H₂ and IBGCC-MeOH) and the methanol
435 reactor product (in IBGCC-MeOH plant) was extracted to preheat the water used for
436 steam generation.

437 The net energy from the IBGCC-MeOH plant (including waste heat and heat and
438 power generation for other biorefinery processes) was 0.35 PJ y⁻¹ as power, 0.16 PJ
439 y⁻¹ as heat and 0.26 PJ y⁻¹ as methanol (HHV of 22.7 MJ kg⁻¹). Thus, the operating
440 energy efficiency of IBGCC-MeOH plant is 42.3%, based on HHV of husk.
441 Similarly, the net energy produced from IBGCC-H₂ plant was 0.32 PJ y⁻¹ as power,
442 0.04 PJ y⁻¹ as heat and 0.4 PJ y⁻¹, as hydrogen. Thus, the operating energy efficiency
443 of IBGCC-H₂ plant is 41.8%.

444 The CPE is reduced from 2.67 PJ y⁻¹ in the standalone biodiesel production system
445 to 2.15 PJ y⁻¹ in the integrated system, resulting in further CPE saving by 19%. The
446 total GWP impact (as CO₂-eq) is reduced from 266.9 Gg y⁻¹ to 211.2 Gg y⁻¹ (21%
447 reduction) in the integrated biorefinery compared to standalone biodiesel production
448 system.

449 The CPE is reduced from 2.89 PJ y⁻¹ in the standalone green diesel production
450 system to 2.15 PJ y⁻¹ in the integrated system, resulting in CPE saving by 25%. The
451 total GWP impact (as CO₂-eq) is reduced from 258.9 Gg y⁻¹ to 211.2 Gg y⁻¹ (18%
452 reduction) in the integrated biorefinery compared to standalone green diesel
453 production system.

454 An excess power of 0.28 PJ y⁻¹ in the biodiesel system and 0.23 PJ y⁻¹ in the green
455 diesel system can be exported to grid. The overall CPE and GWP savings from
456 integrated biodiesel system with respect to fossil based diesel are increased to 95%
457 and 72% and those from integrated green diesel system are increased to 92% and
458 70%, respectively.

459 The integrated biorefinery systems were self-sufficient in energy and methanol or
460 hydrogen requirements. There is a greater saving from replacement of methanol and
461 especially heat and power in the integrated biodiesel system. However, the green
462 diesel system is more suitable for integration with crude oil-based refinery
463 infrastructure and might receive further support especially from oil companies.

464 **4.2 Alternatives for whole *Jatropha* fruit utilisation**

465 The results of total CPE and GWP analyses of the alternatives utilising whole fruit
466 *Jatropha* in the biodiesel and green diesel integrated biorefinery systems are shown in
467 **Figure 9**. The results are compared against the corresponding standalone systems.
468 The use of the fruit shell as fuel in alternative 2 brings the same benefits as the cake

469 in alternative 1. This allows the utilisation of the cake as fertiliser in alternative 2 and
470 as animal feed in alternative 3. However, alternative 3 achieves more profound
471 improvements due to higher avoided GHG emissions from replacement of soy meal
472 by the Jatropha cake. Integrated system in alternative 2 can reduce the CPE to almost
473 zero. Compared to alternative 2, alternative 3 shows higher fossil resource saving.
474 Systems in alternatives 1 to 3 produce the same total bioenergy output of 4.44 PJ y^{-1}
475 in the biodiesel system and of 4.67 PJ y^{-1} in the green diesel system. In both
476 biodiesel and green diesel systems the change from a positive to a negative CPE and
477 GWP is remarkable when the AD-to-power plant is considered for alternatives 4 and
478 5.

479 **Fig. 9** CPE and GWP comparisons between the stand alone plants and the five
480 integrated alternatives

481 Alternative 4 utilises Jatropha by-products (cake, shell, glycerol) for electricity
482 production through anaerobic digestion. The substitution of grid electricity by biogas
483 electricity resulted in further CPE savings and GWP reduction. The total bioenergy
484 production in the biodiesel system is 5.33 PJ y^{-1} while the green diesel system
485 produces 5.71 PJ y^{-1} . However, as shown in Fig. 9 more benefits in terms of CPE
486 and GWP are obtained in alternative 5.

487 Alternative 5 assumes that the cake is used to produce heat for oil extraction and seed
488 drying while fruit shells and glycerol (biodiesel system) are used to generate power
489 via anaerobic digestion into biogas. In this integrated biodiesel system, 5.05 PJ y^{-1} of
490 output energy is generated in the form of biodiesel and CHP. The total input energy
491 is 9.45 PJ y^{-1} from Jatropha fruit fractions and 0.14 PJ y^{-1} from diesel used in field
492 operations during cultivation, yielding an overall efficiency of 53%. This is an
493 increase by 14% from the Jatropha oil conversion to biodiesel in the standalone

494 process. In the green diesel system, the output energy is 5.43 PJ y^{-1} in the form of
495 green diesel, propane fuel and CHP from the same total input energy as in the
496 biodiesel system, resulting in an overall efficiency of 57%, which is 16% more
497 efficient than the *Jatropha* oil conversion to green diesel in the standalone process.
498 Both systems exhibit a land to energy yield of 83 GJ ha^{-1} and the GWP ($\text{CO}_2\text{-eq.}$). In
499 both biofuel systems the GWP of the net bioenergy produced is 149 Gg y^{-1} . Thus the
500 average GWP per unit of bioenergy is 29 g MJ^{-1} . This GWP value is before
501 accounting credits from displacement of fossil-based energy by the excess bioenergy
502 exported from the biorefineries. After accounting the respective credits from
503 replacement of grid electricity (and LPG in the green diesel system) and allocating
504 the impacts to biodiesel or green diesel energy, the CPE saving is 138% and GWP
505 reduction is 114% in the biodiesel system while the CPE saving is 133% and GWP
506 reduction is 111% in the green diesel system, respectively. These savings are more
507 than two-fold compared to the standalone systems. These imply that, although it
508 might not be possible to completely de-carbonise the biofuel supply chains upstream
509 (e.g. in the cultivation stage where extensive fertilisation is required to increase
510 yields), the impacts can be counterbalanced by whole crop conversion into useful
511 products in integrated biorefinery systems as in the alternative 5.

512 **5. Conclusions**

513 Comprehensive system modelling, simulation, integration and analysis tools have
514 been shown for environmentally more viable integrated biorefinery configurations
515 aimed at high efficiency biofuel and energy productions. The low energy efficiency
516 of the standalone biofuel systems can be improved by converting the whole fruit into
517 energy products by in-process production of methanol or hydrogen and CHP for the
518 various processes. Thus, the strategic utilisation of seed husk in IBGCC systems has

519 been explored for reduction in GWP and CPE, being significantly higher than shown
520 in previous studies. By following a total site utility system design approach,
521 integrated biorefinery systems can be designed to be self-sufficient in terms of
522 energy and chemical supply. Potential benefits from the use of Jatropha cake as fuel
523 or animal feed can be obtained. The GWP savings are favoured by the utilisation of
524 cake as animal feed, whilst its utilisation as fuel favours fossil primary energy
525 savings. Additionally, the integration of anaerobic digestion of Jatropha fruit shells,
526 cake and/or glycerol producing biogas used for power generation has also shown
527 enhanced savings. The two biofuel systems studied had very similar performance
528 regarding GWP and CPE savings. Findings from this work combined with an
529 economic analysis would allow a holistic selection of the best integrated biorefinery
530 configuration.

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Table 1 Elemental analysis, compositions and calorific values of various Jatropha products

	FRUIT		SEED		KERNEL	
	Shell	Seed	Husk	Kernel	Oil	Cake
Mass (%)	31.0	69.0	33.7	66.3	58.2	41.8
C	32.52	60.71	48.5	66.92	77.40	52.3
H		8.19	5.7	9.46	11.58	6.5
O		25.33	41.0	17.35	11.01	26.18
N	3.64	1.67	0.67	2.17		4.81
S	0.02	0.16	0.01	0.24		0.58
P	0.76					2.23
K	4.93					1.5
Ash	14.88	3.93	4.08	3.86		9.24
HHV (MJ kg ⁻¹)	17.28	27.1	19.9	30.9	39.6	18.3

Table 2 CPE and GWP (as CO₂-eq) factors for materials and energy used or produced in the various Jatropha subsystems

Item	Functional unit	CPE (MJ)	GWP (g)	Reference
N fertiliser (Urea)	kg	49.25	2940	[45]
P fertiliser (Triple superphosphate)	kg	18.81	1160	[45]
K fertiliser	kg	5.6	380	[45]
Machinery (manufacturing and storage)	h	40.81	2.912	[45]
Storage buildings	m ² y	51.69	4.721	[45]
Abamectin (pesticide)	L	190	13.12	[45]
Glyphosate (herbicide)	L	190	13.12	[45]
Diesel	MJ	1.114	74.4	[46]
Electricity mix	MJ	2.597	173.4	Estimated from [50]
Natural gas (NG)	MJ	1.016	61.2	[45]
Liquefied petroleum gas (LPG)	MJ	1.06	76.4	[47]
Fuel Oil	MJ	1.11	94.9	[45]
Hexane	kg	37.5	861	[7]
Methanol	kg	12.872	2836	[33]
Hydrogen	kg	183.2	11888	[48]
Soy meal	kg	4.13	726	[49]

Table 3 Reported measured yields of *Jatropha* plantations in different locations and estimated annual seed yield at maturity [2], [12], [14], [51]

Location	AAR (mm)	Age, A (y)	Reported yield at age A , Y_A (kg/ha)	Yield at maturity, Y_m (kg/ha)
Bawal, India	521	3	208	300
Jaipur, India	668	2.5	313	500
Erode, India	693	2.5	350	550
Kapiri Mposhi, Zambia	744	2.5	500	780
Nashik, India	690.5	5	1200	1200
Hyderabad, India	812.5	3	911	1400
Digini, Mali	1020	2	550	1500
Andhra Pradesh, India	925	2.5	1000	1680
Surabaya, Indonesia	1751	2	1000	1950
Sinaloa, Mexico	600	2	980	1966
Tamil Nadu, India	945	3	1573	2000
Allahabad, India	998	4	2000	2300
Bhavnagar, India	800	2	1270	2400
Tirunelveli, India	736.9	3	2000	2600
Leon, Nicaragua	1593	4	2500	2750
Managua, Nicaragua	1200	4	3484	3915
Paraguay	1370	8	4000	4000
Sinaloa, Mexico	1453	2	2040	4092
Thailand	1470	1	794	5456
Maximum	1500			5000

Table 4 Parametric coefficients for correlation of Jatropha seed yield at maturity to average annual rain fall (Eq. 2) and nitrogen fertilisation (Eq. 3)

coefficient	Eq. 2	coefficient	Eq. 3
a_1	-5.6163×10^{-6}	b_1	2142
a_2	1.3663×10^{-2}	b_2	0.046
a_3	5.2481	b_3	1.096

Table 5 Inventory data for Jatropha cultivation in the location under study (Personal communication from one of the authors, Dr. Jorge Martinez-Herrera)

Inventory	Amount input
N fertiliser	162 kg/ha
P fertiliser	162 kg/ha
K fertiliser	162 kg/ha
Machinery	2h/ha, 42.6 kW tractor
Diesel	6584 MJ/ha
Electricity from grid	27.8 MJ/ha
Storage area	3.7 m ² /ha
Abamectin (pesticide)	2 L/ha
Glyphosate (herbicide)	2 L/ha

Table 6 Specifications for the biodiesel simulation in Aspen Plus

Equipment	Aspen model	T (°C)	P (kPa)	Other specifications		Reference
RMIXHTR	Heater	70	101.3			[4]
TEREACT	Rstoic	70	101.3	TG conversion fraction	0.93	[4]
				FFA conversion fraction	1	Assumed
MEOHREC	RadFrac		40	Pressure drop (bar)	0.1	Assumed
				Stages	16	From simulation
				Methanol mass recovery (%)	99	Specified
				Molar reflux ratio	2	From simulation
RECPUMP	Pump		200			
COOL1	Heater	25	101.3			
DECANT	Decanter	25	101.3			
BIODREC	RadFrac		101.3	Stages	4	From simulation
				FAME mass recovery (%)	99	Specified
				Molar reflux ratio	0.2	From simulation
PREH1	Heater		101.3	Duty (MW)	2.27	From simulation
PREH1-1	Heater	35	101.3			Specified
COOL2	Heater	35	101.3			Specified

Table 7 Specifications for the green diesel simulation in Aspen Plus [7]

Equipment	Model	T (°C)	P (kPa)	Other specifications	
HE1	HeatX			Hot Stream Outlet T (°C)	275
RMIXHTR	Heater	188	3450		
H2TRECTR	RYield	325	3450	Mass yield fractions:	
				GDIESEL	0.8415
				PROPANE	0.0290
				WATER	0.0213
				CO ₂	0.1063
				H ₂	0.0020
OILPUMP	Pump		3450	Isentropic efficiency	0.85
PHASESEP	Flash2	35	1200	Free water phase valid	
PSA	Sep			Component mass split fraction:	
				CO ₂ in stream CO2	1
				PROPANE in stream CO2	0
				H ₂ in stream H2RECVD	1
				Others in stream H2RECVD	0
GDISLREC	RadFrac		101.3	Stages	8
				No condenser, no reboiler	
LPGSEP	Flash2	20	101.3	Free water phase valid	
H2FCOMPR	Compresor		3450	Isentropic efficiency	0.85
H2RCOMPR	Compresor		3450	Isentropic efficiency	0.85

Table 8 Specifications for the husk to CHP and methanol or CHP and hydrogen simulations

Name	Model	T (°C)	P (MPa)	Other specifications	
AIRCOMPR	Compr		3	Isentropic efficiency	0.85
MPRODEXP	Compr		4.1	Isentropic efficiency	0.9
OFFGCOMP	Compr		3	Isentropic efficiency	0.85
B1	Fsplit			Flow rate (t d^{-1}) for steam to biomass ratio =0.35 in IBGCC-MeOH	94.93
				Mass split fraction in IBGCC-H ₂	1
B5	Flash2	55	0.1		
RECWPUMP	Pump		3	Isentropic efficiency	0.85
B19	Fsplit			Mass split fraction (IBGCC-MeOH)	0.2384
COMBUSTR	RGibbs	1200	3		
CYCLONE	SSplit			Ash mass split fraction	1
EFFLUSEP	Flash2	55	3		
GCLEANUP	Sep2	55	3	CO ₂ mass split fraction	0.9
				H ₂ S and COS mass fraction	1
HRSG1	HeatX			Hot stream outlet T (°C)	450
MEOHREAC	Requil	250	10		
MEOHREC	Flash2	55	3		
STGASIFY	RGibbs	1100	3		
SYNGCOMP	Compr		10	Isentropic efficiency	0.85
SYNGCOOL	Heater	55	3		
WGSR	Requil	450	3		
PSA	Sep			H ₂ mass split fraction	0.8
			0.1	OFFGAS stream flash pressure	

Table 9 LCA results for the biodiesel and green diesel stand alone systems

	Mass flow (Gg y ⁻¹)	Energy (PJ y ⁻¹)	CPE (PJ y ⁻¹)	GWP (Gg y ⁻¹)	CPE (MJ MJ ⁻¹)	GWP (g MJ ⁻¹)
<i>Biodiesel system</i>						
Total before credits	100.0	3.96	2.67	266.9		
Net glycerol credit	10.7	0.20	-0.23	-19.3		
Net cake credit	75.1		-0.43	-76.4		
Net to biodiesel			2.0	171.5	0.51	43.3
<i>Green diesel system</i>						
Total before credits	93.4	4.28	2.89	258.9		
Net propane fuel credit	3.4	0.16	-0.17	-12.0		
Net cake credit	75.1		-0.43	-76.3		
Net to green diesel			2.29	170.6	0.53	39.9

Figure captions

Fig. 1 Overview of the integrated Jatropha biorefinery systems for the production of biodiesel and green diesel with utilities and auxiliary raw materials generated from Jatropha by-products. Numbers 1–5 indicate in which alternative the options for by-product utilization are selected. Mass flow rate in Gg y^{-1} , Heat and power in PJ y^{-1} . IBGCC: Integrated biomass gasification and combined cycle

Fig. 2 The Jatropha cultivation system producing seeds conditioned in field

Fig. 3 Simulation of biodiesel production plant by heterogeneous transesterification of Jatropha oil

Fig. 4 Simulation of green diesel production plant by hydrotreatment of Jatropha oil

Fig. 5 Simulation of Jatropha seed husk IBGCC-MeOH plant

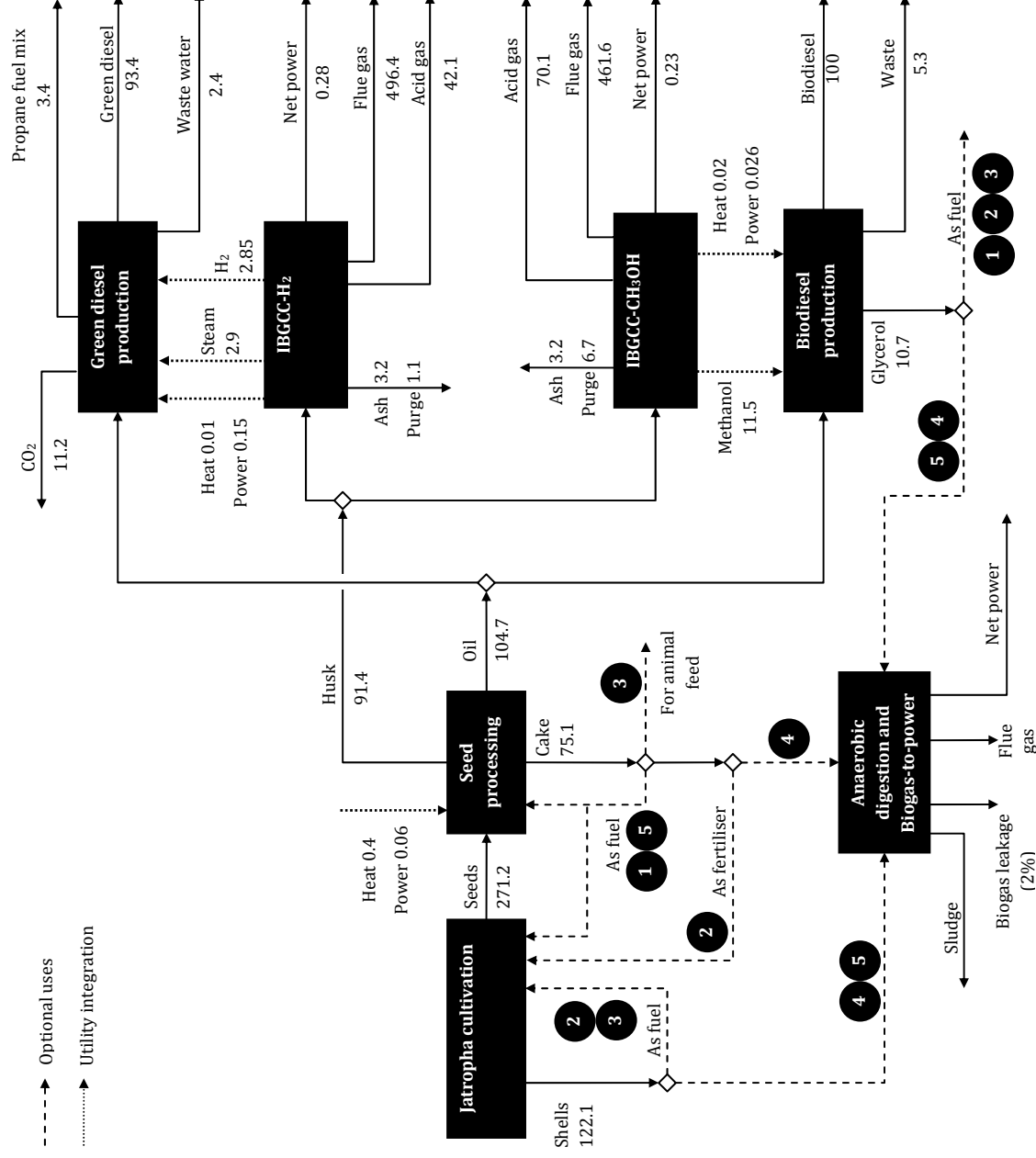
Fig. 6 Simulation of Jatropha seed husk IBGCC- H_2 plant

Fig. 7 Results of CPE and GWP impacts from Jatropha cultivation

Fig. 8 CHP network of husk processing into a) IBGCC-MeOH and b) IBGCC- H_2

Fig. 9 a) CPE and b) GWP comparisons between the stand alone plants and the five integrated alternatives

Fig. 1 Overview of the integrated Jatropa biorefinery systems for the production of biodiesel and green diesel with utilities and auxiliary raw materials generated from Jatropa by-products. Numbers 1–5 indicate in which alternative the options for by-product utilization are selected. Mass flow rate in Gg y^{-1} , Heat and power in PJ y^{-1} . IBGCC: Integrated biomass gasification and combined cycle



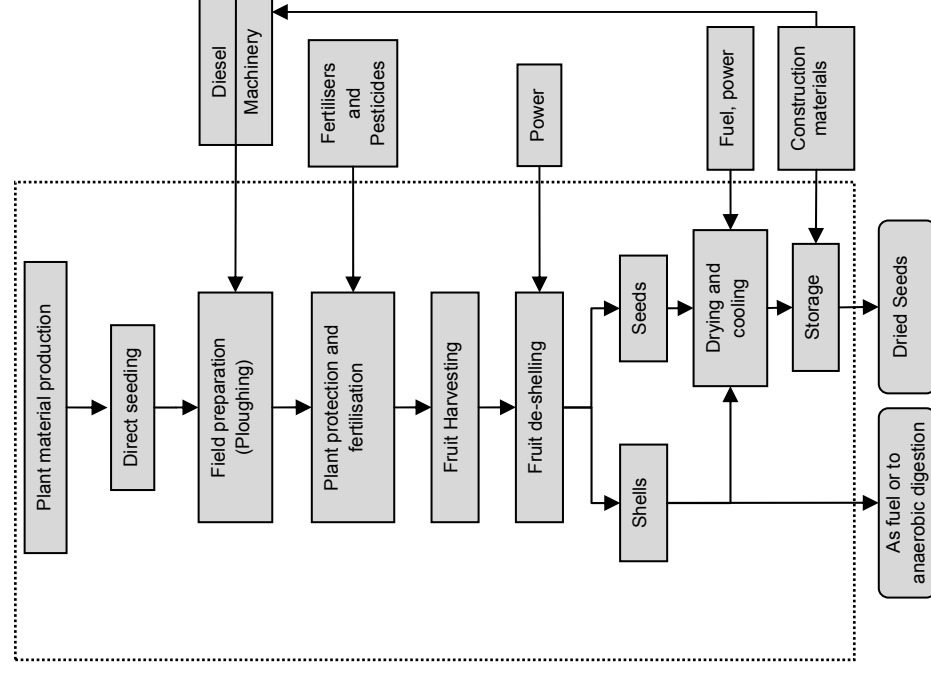


Fig. 2 The Jatropha cultivation system producing seeds conditioned in field

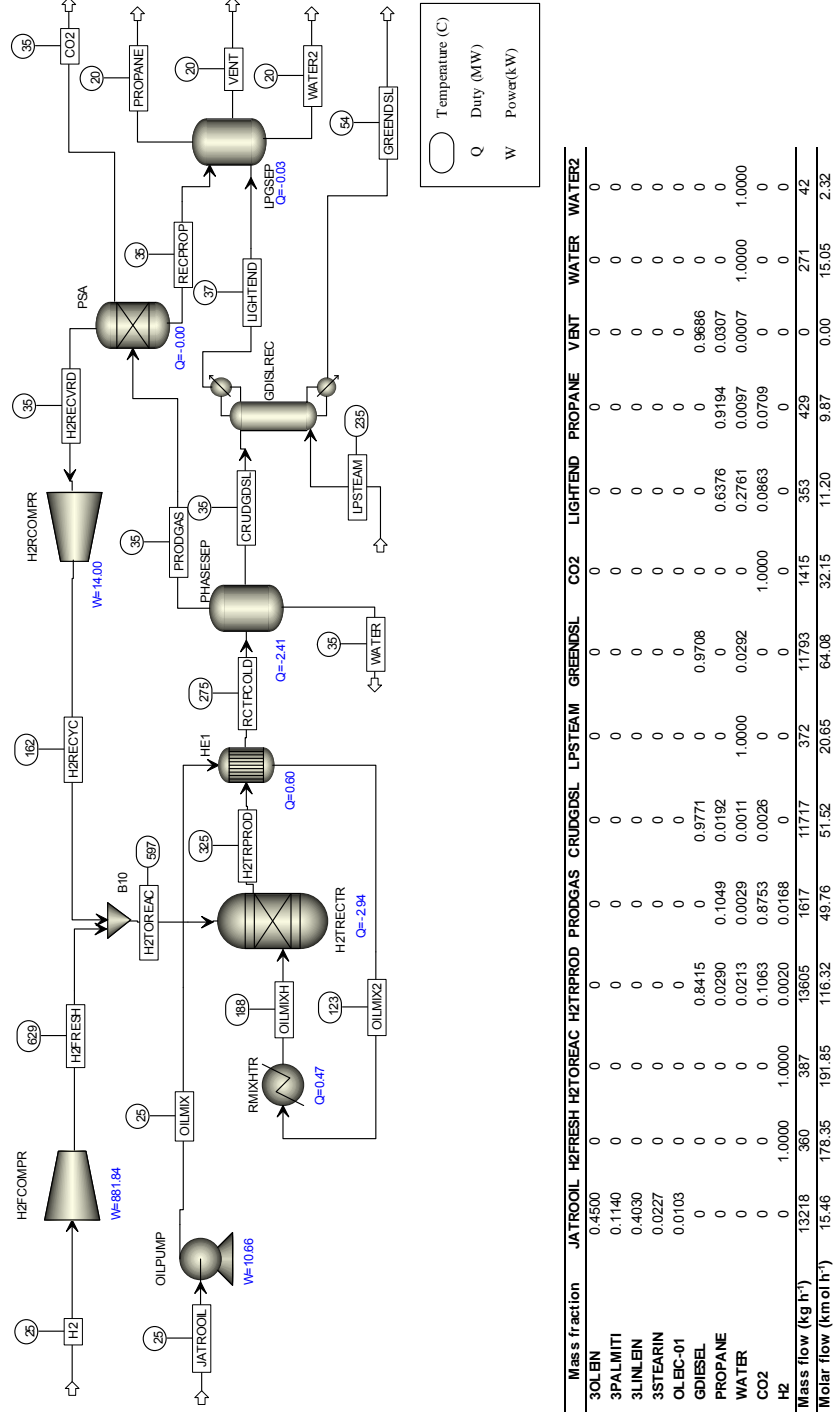
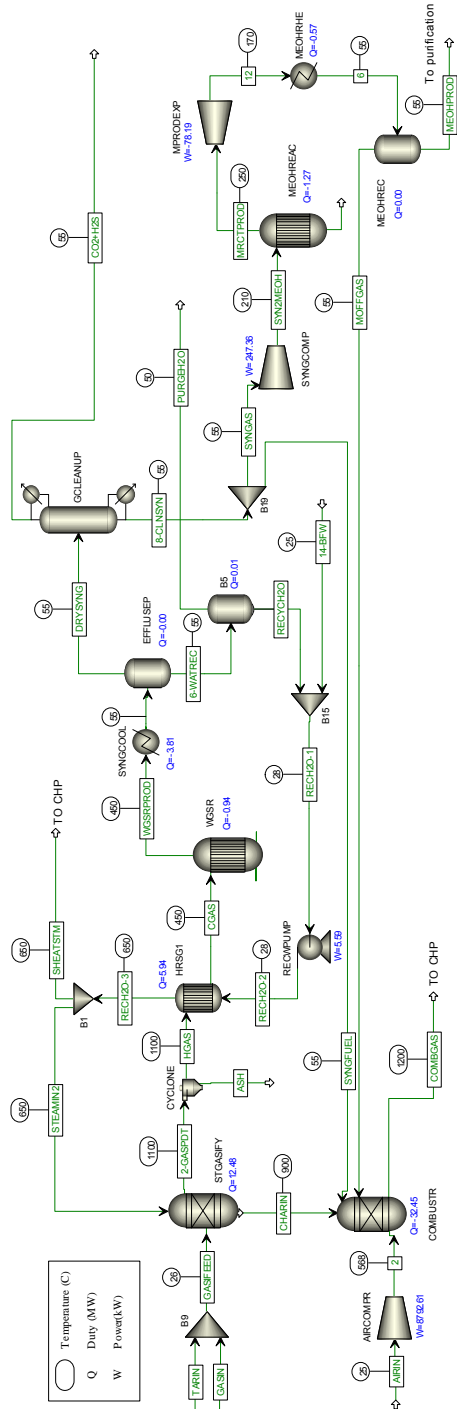
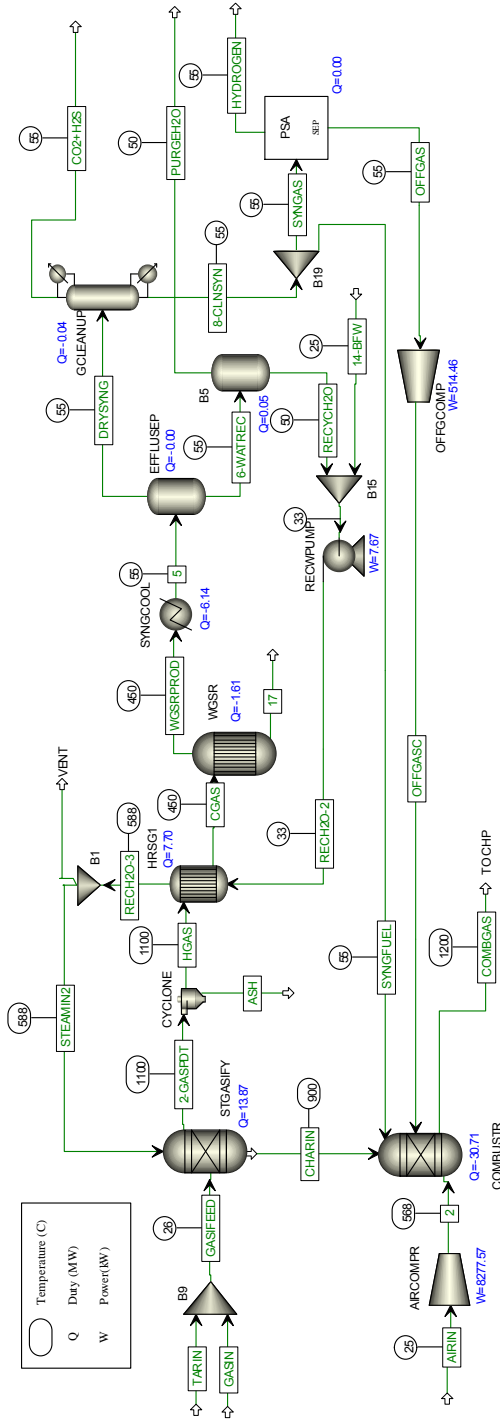


Fig. 4 Simulation of green diesel production plant by hydrotreatment of Jatropha oil



Mass fraction	CHARIN	GASIN	TARIN	2-GASPTD	ASH	WGSRRPROD	REC/CYH2O	PURGEH2O	STEAMING	DRYING	CO2+H2S	8-CLNSYN	SYNGFUEL	SYNGAS	MEORPROD	MOFFGAS	COMBGAS	ARIN	14-BFW	SHEATSTM
H2O	0	0.1667	0.1428	0.1564	0	0.0486	0.9587	0.0567	0.9665	0.0065	0	0.0105	0.0105	0.0105	0.0027	0.0001	0.1304	0	1	0.8955
N2	0	0.0129	0	0.0046	0	0.0047	0	0.0007	0	0.0050	0	0.0081	0.0081	0.0081	0.0004	0.0328	0.6770	0.7871	0	0
O2	0	0	0.2983	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0205	0.2329	0	0
NO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4.98E-06	0	0	0
NO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0003	0	0	0
S	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SO3	0	0.0033	0	0.0589	0	0.0730	0	0	0.0772	0	0.1253	0.1253	0.1253	0	0	0	0	0	0	0
H2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.1399	0	0	0	0
C	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO	0	0.4486	0	0.6095	0	0.4539	0.0003	0.0896	0	0.4790	0	0.7776	0.7776	0.7776	0.0066	0.4805	0	0	0	0
CO2	0	0.0839	0	0.1380	0	0.4130	0.0387	0.8455	0.0045	0.4266	0.9998	0.9992	0.9992	0.9992	0.0427	0.2400	0.1718	0	0	0.0045
H2S	0	0.0002	0	0.0001	0	0.0001	0	0.0002	0	0.0001	0.0002	0	0	0	0	0	0	0	0	0
CH4	0	0.0500	0	0.0553	0	0.0555	0	0.0073	0	0.0057	0	0.0063	0.0063	0.0063	0.0031	0.0291	0	0	0	0
COS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ETHAN-01	0	0.2544	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
METHANOL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ASH	0	0	0	0.0272	1	0	0	0	0	0	0	0	0	0	0	0.1945	0	0	0	0
MeOH flow (kg h ⁻¹)	443	5336	5194	13566	489	14647	668	154	3956	13594	5320	8534	6500	2035	1549	465	62589	55162	5188	1891
MeOH flow (kmol h ⁻¹)	36.94	215.63	128.30	953.07	953.07	953.07	36.89	3.50	213.69	913.88	120.88	793.00	603.95	189.05	48.09	47.28	2250.66	1912.00	288.00	104.69

Fig. 5 Simulation of Jatropha seed husk IBGCC-MeOH plant



Mass fraction	CHARIN	GASIN	TARIN	2-GASRDT	ASH	WSRPROD	RECYCHO	PURGEH2O	STEAMING2	DRYSNG	CO2+H2S	8-CLNSYN	SYNGFUEL	SYNGAS	HYDROGEN	OFFGAS	COMBGAS	AIRIN	14-BFW
H2O	0	0.1667	0.1428	0.2895	0	0.1465	0.9553	0	0.0543	0.9848	0.0064	0	0.0153	0.0153	0	0.0183	0.1463	0	1
N2	0	0.0129	0	0.0036	0	0.0037	0	0	0	0	0.0045	0	0.0110	0.0110	0	0.0131	0.6845	0.7671	0
O2	0	0	0.2983	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0204	0.2329	0
NO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4.54E-06	0	0
NO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0003	0	0
S	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H2	0	0.0033	0	0.0516	0	0.0695	0	0	0	0.0659	0	0.2069	0.2069	0.2069	1.0000	0.0496	0	0	0
C	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO	0	0.4486	0	0.4278	0	0.2049	0.0001	0.0315	0	0.2515	0	0.6060	0.6060	0.6060	0	0.7263	0	0	0
CO2	0	0.0639	0	0.2045	0	0.5739	0.0445	0.9121	0.0151	0.6500	0.9999	0.1567	0.1567	0.1567	0	0.1877	0.1484	0	0
H2S	0	0.0002	0	0.0001	0	0.0001	0	0.0001	0	0.0001	0.0001	0	0.0001	0	0	0	0	0	0
CH4	0	0.0500	0	0.0014	0	0.0015	0	0.0015	0	0.0017	0	0.0041	0.0041	0.0041	0	0.0049	0	0	0
COS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ETHAN-01	0	0.2544	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PHENOL-01	0	0	0.4379	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
METHANOL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ASH	0	0	0.0710	0.0214	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mass flow (kg h ⁻¹)	443	5336	5764	19099	409	18690	2717	851	7999	15123	8948	6275	4083	2162	361	1821	58287	51931	5283
Molar flow (kmol h ⁻¹)	36.84	215.63	129.30	1180.73	1180.73	1180.73	146.81	21.25	440.06	1012.67	201.05	811.61	529.39	282.23	179.19	103.04	2132.08	1800.00	293.27

Fig. 6 Simulation of Jatropha seed husk IBGCC-H₂ plant

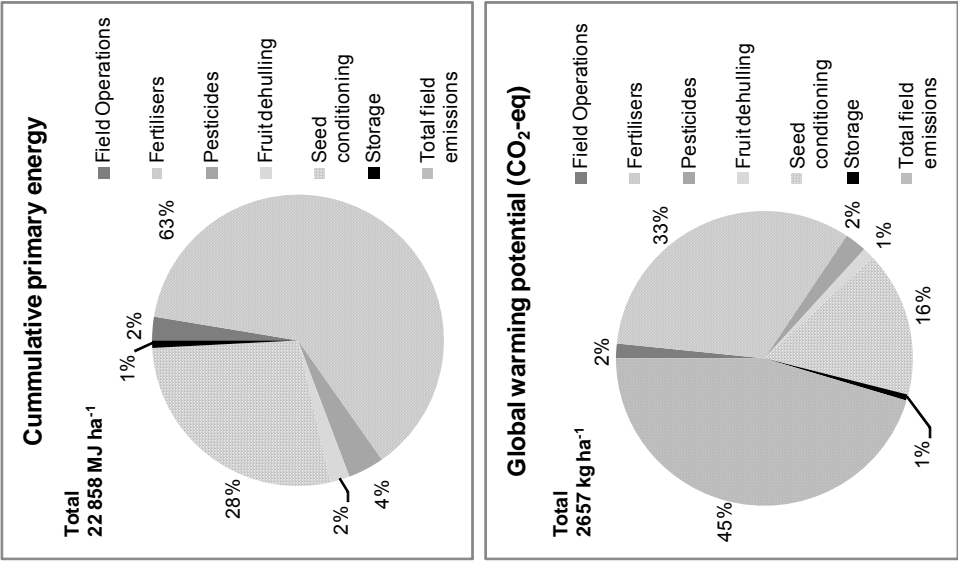
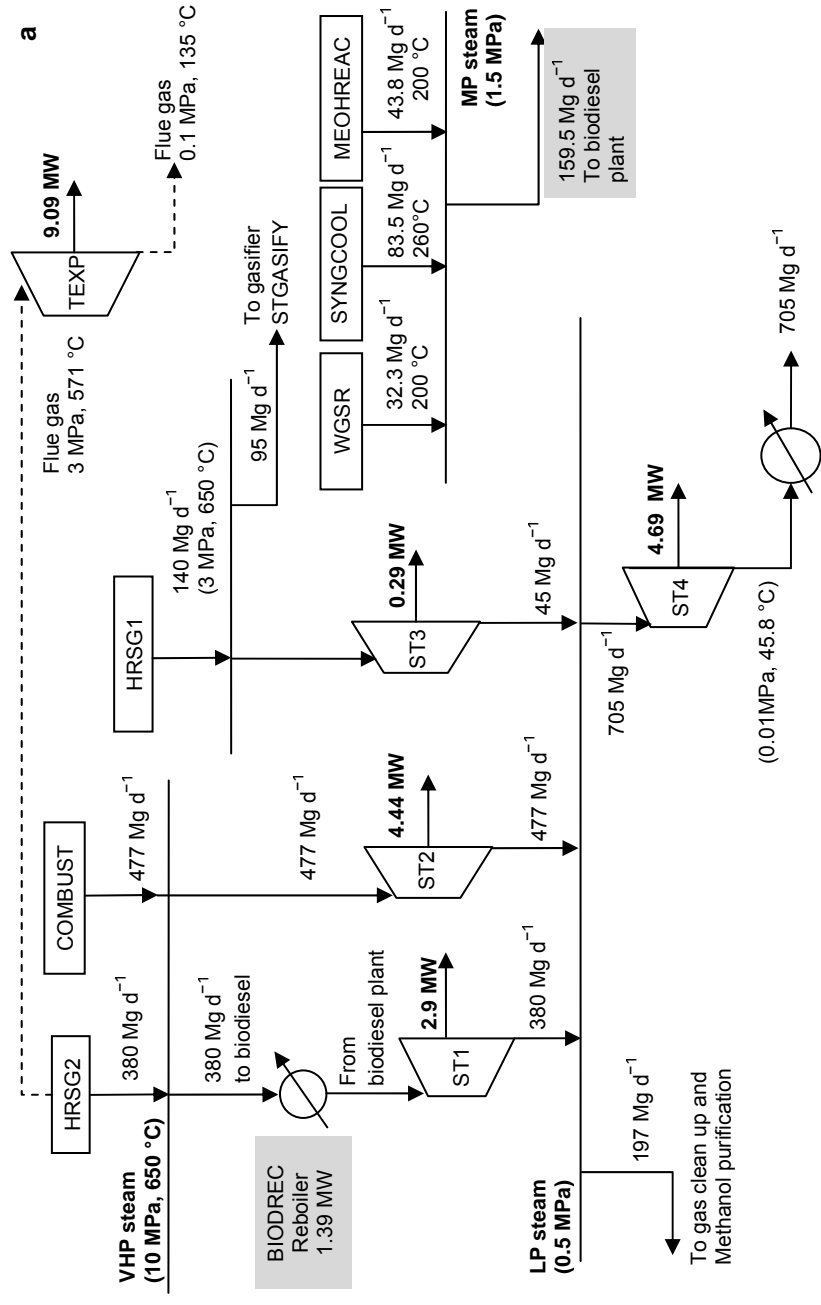
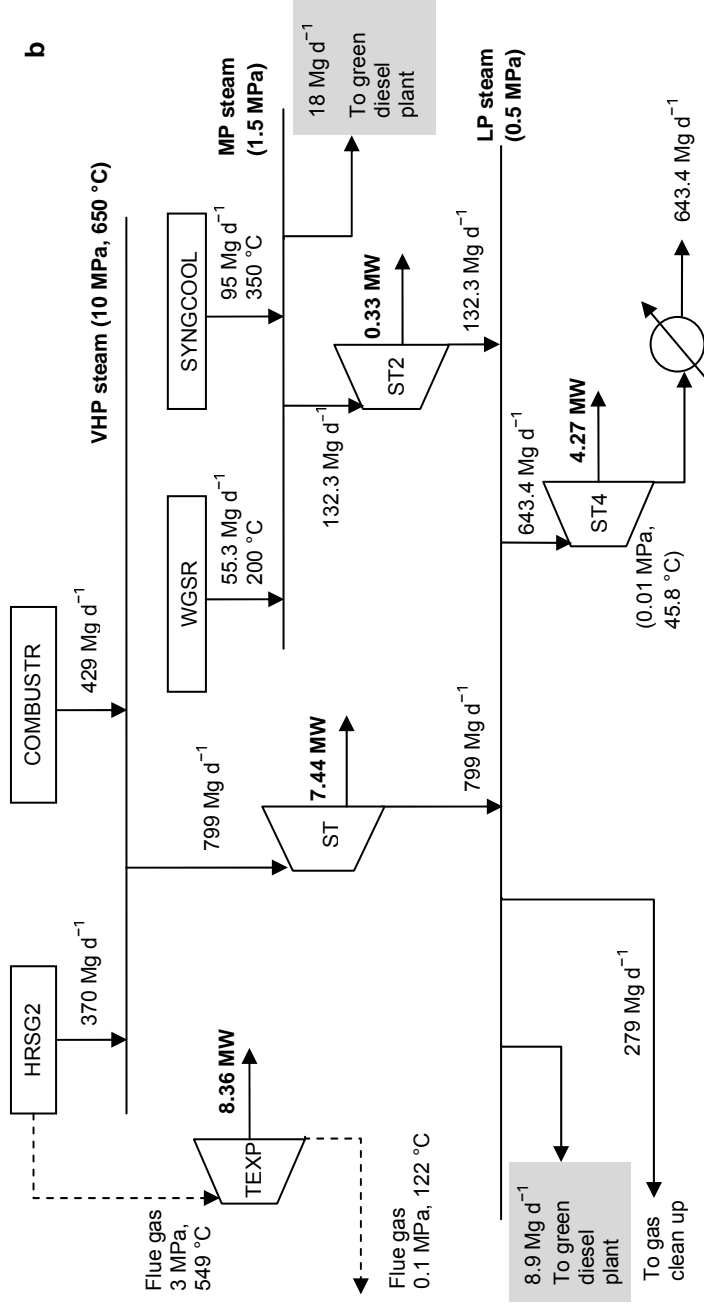


Fig. 7 Results of CPE and GWP impacts from Jatropha cultivation





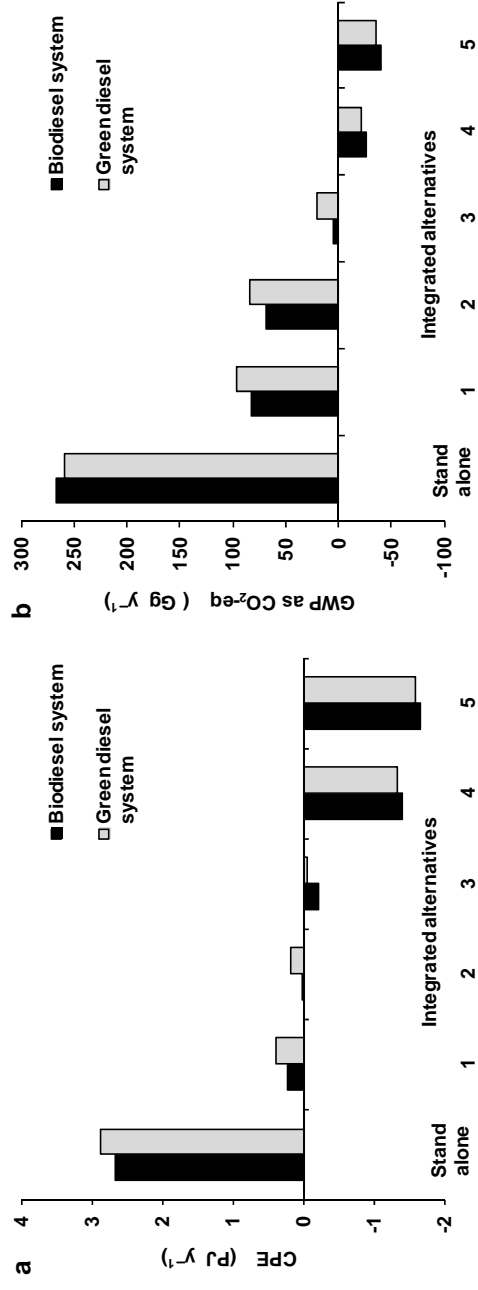


Fig. 9 a) CPE and b) GWP comparisons between the stand alone plants and the five integrated alternatives

APPENDIX A

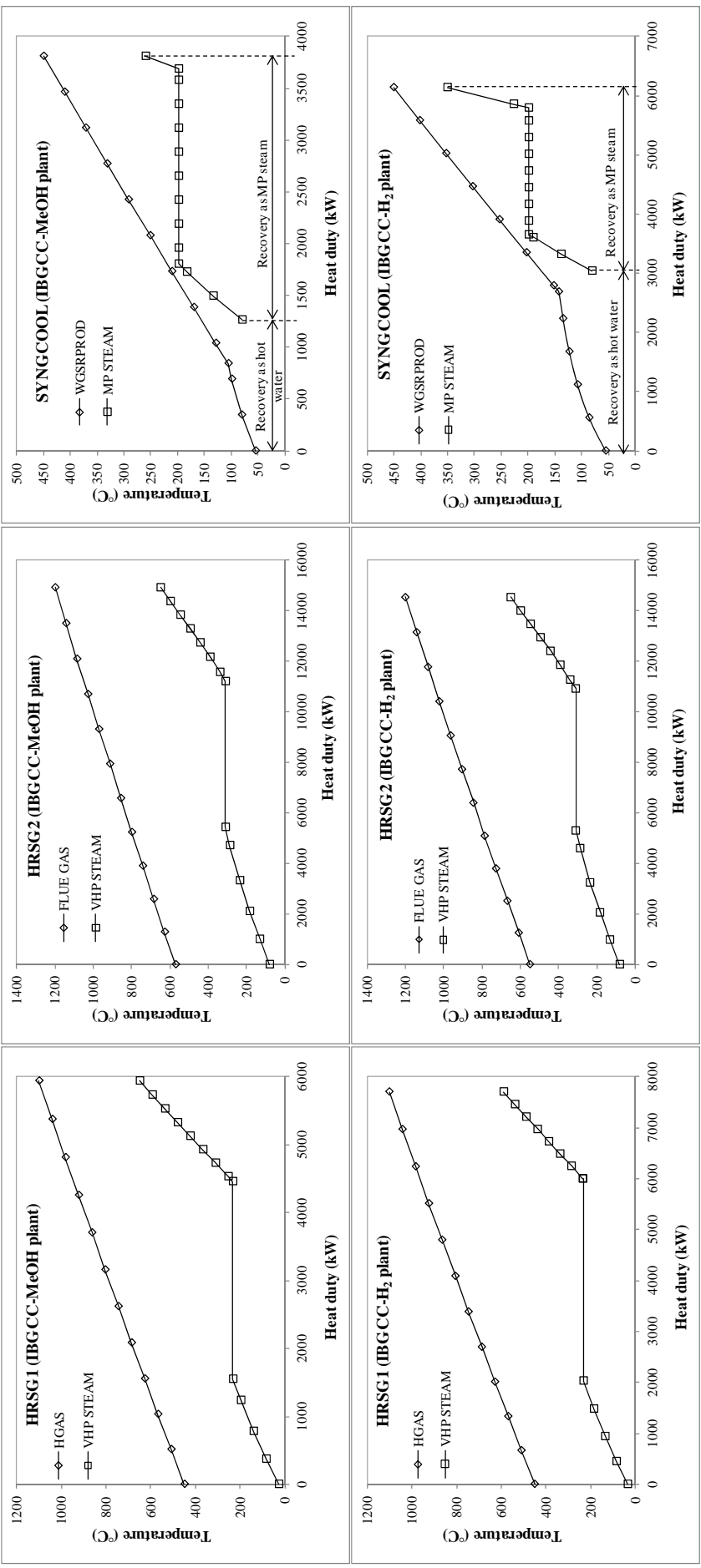
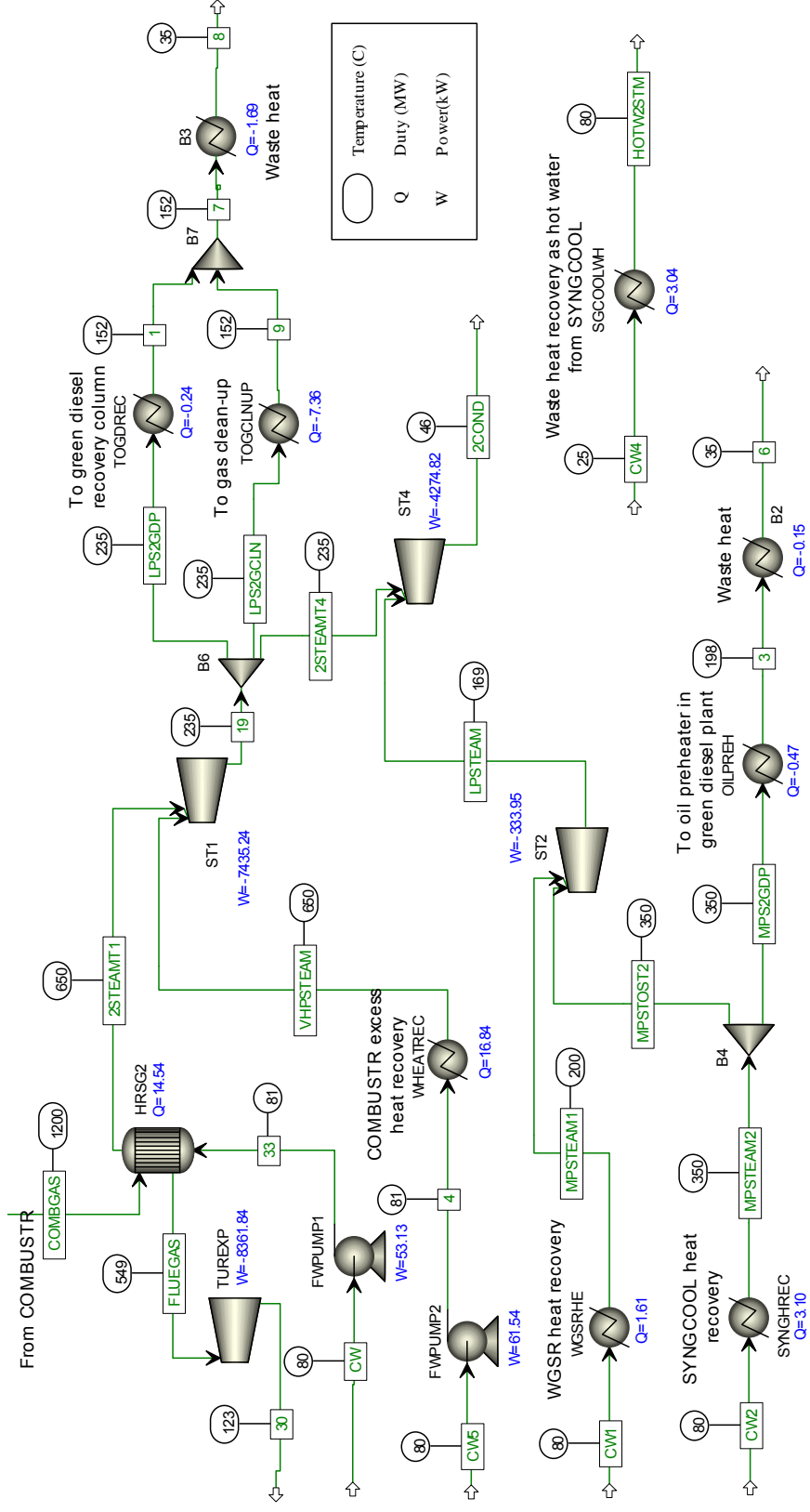


Fig. A.1 Composite curve analysis for determining the amount of steam generation from HRSG1, HRSG2 and SYNGCOOL in the CHP network of the IBGCC-MeOH and IBGCC-H₂ plants



Chapter 5

A method for combined Economic Value and Environmental Impact analysis

5.1 Preamble

Designing a biorefinery to meet both economic and environmental objectives is a challenging task due to a wide range of alternatives for pre-treatment and conversion processes and the trade-offs that might result while trying to integrate various process pathways. It is essential to be able to identify the most promising process pathways to prioritise for integration into the biorefinery process network. The value analysis approach by Sadhukhan (2002) is a robust tool developed for economic analysis and optimisation of a process network (Sadhukhan et al., 2003; Sadhukhan and Smith, 2007). It enables evaluation and graphical presentation of economic contributions from individual elements forming a process network (streams, process units, paths, trees). An approach combining economic value and environmental impact (EI) assessments has been further developed to analyse the potential EI *savings margin* of a biorefinery (Martinez-Hernandez et al., 2012). The full paper invited for publication, presented here, was published in the Journal of Chemical Engineering Research and Design.

The basic data input for value analysis are the costs of feedstock, auxiliary raw materials and utilities and prices of products. Equivalent differential modelling can be done for each primary environmental impact category. There is a corresponding and analogous *EI cost* of feedstock, auxiliary raw materials and utilities. However, whilst economic costs and prices are driven by the market, EI costs and values need to be determined by environmental footprint or life cycle analysis (LCA) methods. It is possible to develop an equivalent concept to value on

processing of streams, i.e. their *EI credit values*. An *EI credit value* of a product is the impact saving from the displacement of a fossil-based product by an equivalent biorefinery product. The established correspondence between economic and EI variables gives light for the systematisation of a combined Economic Value and Environmental Impact (EVEI) analysis methodology presented in this paper.

5.2 Discussion of publication 4

The EVEI analysis is a tool that emerges from the combination of the power of the value analysis methodology for the evaluation of economic potential and LCA for EI analysis. The fundamentals of the methodology are presented in the paper and the calculation procedures are demonstrated by taking the standalone bioethanol plant studied in Chapter 2 as a case study.

The paper presents the stand-alone bioethanol plant presented in Chapter 3 and the biorefinery including the arabinoxylan co-production process studied in Chapter 2. Although the results in terms of GHG emissions saving are similar to those found in Chapter 3, the new methodology provides insights into the differential economic and environmental performances of individual elements in a process network, directing to network hot spots analysis. The development of the economic and environmental stream profiles helps to understand how the EI and economic costs and benefits are distributed throughout a process network. The stream profiles also help to identify trade-offs between profitability and the environmental footprint of streams when a co-production pathway is integrated in a biorefinery. Variations in the market prices of feedstock and products as well as in the feedstock production systems can be easily tracked. Furthermore, any impact category or a weighted factor for various categories could be used as indicator for environmental performance. Policy drivers (European Union, 2009; US Congress 2007) can be also incorporated to analyse biorefinery technology and product sustainability and to identify process improvement and optimisation opportunities, as shown in Chapter 6.

Overall, the paper presents a robust tool that has proved to be effective for the combined analysis of economics and EI performances of biorefineries, to clarify and facilitate the trade-offs between these objectives. The combined evaluations and

insights into trade-offs offer potential application for the ranking of various processing pathways in order to select the best alternatives for process design.

Methodological aspects

Figure 5.1 shows the framework for the EVEI analysis methodology which includes the multilevel approach presented in Chapter 4. The methodology has been implemented and integrated into a computer-aided tool in the Excel environment, with all calculations performed in the VBA platform. The tool was used to perform mass and energy balances of the system, the EVEI analysis calculations and presentation of results as described in the publication. The mass and energy balances of the bioethanol production process is presented in Figure 3 of the publication, which also correspond to the balances already presented in the publication 2 of Chapter 3. More detailed balance tables are provided in Tables A-B of the Appendix.

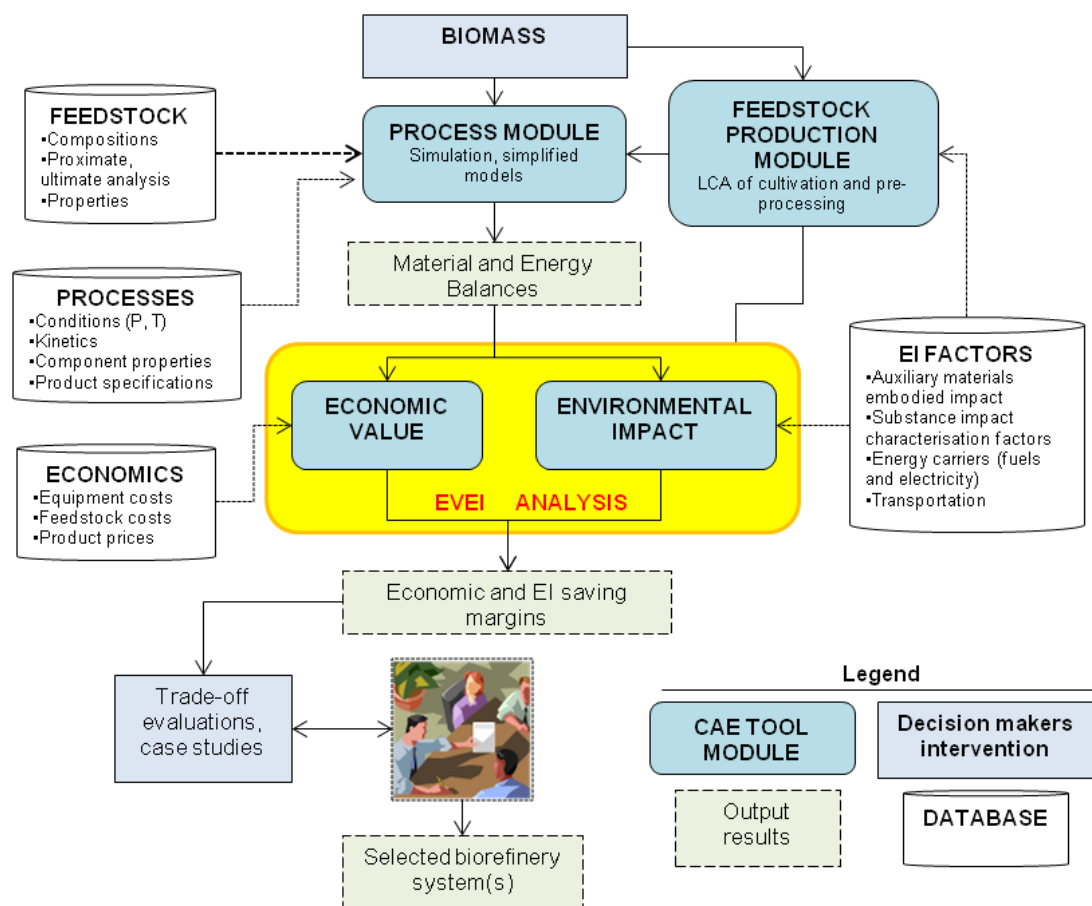


Figure 5.1 Framework for economic value and environmental impact (EVEI) analysis of biorefinery systems which includes a multilevel modelling approach integrated into a computer aided engineering (CAE) tool.

The process models developed in process simulation software can be linked to the EVEI calculations or simplified to linear correlations in a spreadsheet. For the purposes of presentation of the EVEI methodology for a hypothetical biorefinery, the use of the simplified models is justified. For a more detailed study and for other specific purposes (e.g. analysis of existing plant data, optimisation, etc.), the use of more explicit and complex models is recommended to obtain more accurate representation of the processes. The simplicity and robustness of the EVEI analysis methodology can easily accommodate models at any level of detail. This will allow carrying out overall optimisation using the capabilities of the methodology to capture variability in the process, economic and environmental variables in the EVEI modelling of the process streams, as shown in the publication.

A key aspect of the EVEI analysis methodology is how the allocation of costs and environmental impact is carried out. First, due to the calculation of economic and environmental variables at each process unit, the allocation is made at the process unit level and not at the overall system level as in a typical LCA study (Gnansounou et al., 2008). This decreases the level of uncertainty and captures the structure of a product pathway in a process network. By doing this, allocation is generally reduced to a small number of streams. However, the methodology is not limited to a certain number and can handle any number of streams in a multi-output process unit. Second, any allocation approach could be used in the EVEI analysis methodology, i.e. by mass, by energy content or by economic value. Although mass is a physical quantity easy to interpret, allocation by mass does not reflect the actual value or functionality of a product (Guinée et al., 2002, Gnansounou et al., 2008). Allocation by energy content or calorific value is perfect when only energy products are being produced in a system. Since a biorefinery will produce a wide range of products of different functionality, allocation by energy might not be always suitable. The economic value is considered a more universal quantity since products are evaluated according to their service or function in the real economy (Lim, 2008; Kravanja, 2012). Gnansounou et al. (2008) has shown in a sensitivity analysis that environmental impact results were not sensitive to wheat and bioethanol prices for a wheat-to-ethanol process. Furthermore, Guinée et al. (2002) shows that share on total sales value among the products of a system remain constant in the longer term in spite of price fluctuations. Thus, economic value is the approach used by the EVEI

analysis methodology. This approach provides consistency to the methodology which already calculates the economic value of the streams at every point in the system. This is clearly shown in the publication.

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IChemE

Economic value and environmental impact (EVEI) analysis of biorefinery systems

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ABSTRACT

The selection of product portfolios, processing routes and the combination of technologies to obtain a sustainable biorefinery design according to economic and environmental criteria represents a challenge to process engineering. The aim of this research is to generate a robust methodology that assists process engineers to conceptually optimise the environmental and economic performances of biorefinery systems. A novel economic value and environmental impact (EVEI) analysis methodology is presented in this paper. The EVEI analysis is a tool that emerges from the combination of the value analysis method for the evaluation of economic potential with environmental footprinting for impact analysis. The methodology has been effectively demonstrated by providing insights into the performance of a bioethanol plant as a case study. The systematisation of the methodology allowed its implementation and integration into a computer-aided process engineering (CAPE) tool in the spreadsheet environment.

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Keywords: Biorefinery; Sustainable design; Value analysis; Environmental impact analysis; LCA

1. Introduction

Biorefinery systems have emerged as an attractive route for energy generation, in the form of combined heat and power (CHP) and biofuels, alongside chemical production, with great promise for reduced environmental impact (Kamm and Kamm, 2005; Cherubini et al., 2009). The potential biorefinery market throughout the entire biomass value chain globally has been projected as \$295 billion by 2020 (King, 2010). This estimate includes biorefinery products that could replace fossil-based products that are chemically identical (e.g. ethylene from bioethanol can replace ethylene from natural gas) and those that could substitute for products having similar functionality (e.g. polylactic acid can substitute polyethylene terephthalate used for plastic bottles). The biorefinery concept has been practised widely in the corn wet mill industry, the pulp and paper industry and, more recently, the biofuel industry through the expansion of their product portfolios with value added products in the search for improved process economics and environmental sustainability (Lynd et al., 2005;

Janssen, 2012). To benefit from these advantages, biorefineries must be designed and assessed all the way from factory boundary to system cradle-to-grave in an integrated manner.

Process integration and mathematical optimisation techniques have been applied to handle the complexity of the product allocation problem for biorefineries in terms of economic and environmental impact by Sammons et al. (2008). They proposed an optimisation framework that enabled the inclusion of profitability and other techno-economic metrics to screen at an initial stage those alternatives that maximize profitability. In a second stage, the solutions are assessed using environmental metrics. Sharma et al. (2011) have considered a robust and flexible MILP financial planning model to maximize value for a multi-product multi-platform biorefinery enterprise including a weighting function for tracking the effect of process integration on the CO₂ emissions of the final biorefinery configuration. Tan et al. (2009) proposed an LCA-based modelling framework for fuzzy multi-objective optimisation of three footprint metrics-land use, water and carbon. An LCA-based sustainability multi-scale multi-method approach

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was applied for integrated assessment of material, embodied energy, environmental impact and economic flows and performance by Fahd et al. (2012). A systematic methodology for the design and analysis with respect to cost, operation and sustainability to generate new alternatives with respect to wastewater reduction and efficient downstream separation was proposed by Alvarado-Morales et al. (2009). An approach combining exergy, life cycle and economic analyses was performed for sustainable biofuel production using Aspen Plus™ software by Ojeda et al. (2011). A shortcut method for the synthesis and screening of integrated biorefineries was developed by Bao et al. (2011), wherein a structural representation of chemical species and conversion operator was developed to track individual chemicals allowing for the processing of multiple chemicals in processing technologies. Heyne and Harvey (2013) used the Energy Price and Carbon Balance Scenarios (ENPAC) for comparison of thermodynamic, economic and carbon footprint performances of biorefinery systems. A multi-objective static optimisation framework that included both economical and environmental performance objectives for sustainable biofuel supply chains was proposed by Akgul et al. (2012) to have a complete view of the future implications of biorefinery systems. The various approaches above show how biorefinery assessments have moved from the sole use of techno-economic measures to the inclusion of sustainability metrics useful for decision making in biorefinery design and planning.

The acquisition of measures and of correlations between them in a dynamic manner across the scales is not a trivial task, as it requires applying the sustainability indicators into the design practice (Azapagic and Clift, 1999a, b). As the complexity of the transition from fossil to renewable feedstock arises with more competitive products, processes and technologies, the development of sustainability indicators has led to a list of priorities based on the objectives for such a transition – tackling the global climate change, scarcity of fossil resources and sustainable development. As a result, GHG emissions reduction, fossil energy saving and economic potential of biorefinery products have become important measures that make a biorefinery a plausible alternative to crude oil refineries (Brehmer et al., 2009; Fahd et al., 2012).

Although there have been a number of papers published in the area of biorefinery process design, integration and sustainability indicators, no differential environmental impact analysis of the smallest element (such as a stream associated with a unit operation) to the largest element (such as a whole system) has been proposed so far by means of a unified framework. With the awareness of the significance of integration of sustainability indicators in biorefinery design, there are clear and strengthening imperatives for combining differential economic and environmental emission saving marginal analyses across the scales linking process to systems level variables and design objectives. To this end, this paper presents a robust biorefinery systems analysis tool based on a methodology that combines the concepts of economic value and environmental impact (EVEI) analysis. The marginal economic and environmental impact saving obtained from the products are used as indicators to determine whether a biorefinery system is more sustainable than its fossil-based counterpart system. The methodology adapts environmental impact (EI) analysis techniques (such as life cycle assessment, LCA) to the value analysis methodology (Sadhukhan et al., 2003, 2004, 2008) while extending the differential analysis of network elements (i.e. streams, paths and trees) from the latter methodology to

perform EI analysis. This integrated approach allows decision making regarding environmental and economic considerations at the same time, in order to achieve a sustainable biorefinery design. Section 2 presents methodological aspects of the tool. The tool is then applied to assess a wheat biorefinery system in Section 3.

2. The EVEI analysis methodology

2.1. Economic and environmental impact concepts

The main variables in the EVEI analysis are the economic and EI costs and values. The costs of feedstock (C_f), auxiliary raw materials (C_a) and utilities (C_u) correspond to their market prices or production costs when produced on site. The EI “cost” is the embodied impact incurred during the production and transportation of materials or energy carriers. The end product economic values can be their market prices (V_p). The EI credit (D_p) of a biorefinery product is obtained from the displacement of an equivalent fossil-based product. D_p is a product of the EI cost of the equivalent fossil-based product (I_{peq}) and an equivalency factor β , the amount of fossil-based product displaced per unit amount of the biorefinery product, provided by the relationship in Eq. (1).

$$D_p = \beta \times I_{peq} \quad (1)$$

The concept of credit value, or D_p , indicates the upper bound or limit for the EI cost of a biorefinery product in order to be environmentally advantageous over the fossil counterpart. Subtracting the EI cost from D_p of a biorefinery product yields its EI reduction potential with respect to the equivalent fossil-based product. The resulting EI reduction is termed as EI saving margin, a concept equivalent to economic margin.

Fig. 1 presents the variables used to evaluate the economics and the corresponding variables to evaluate EI of a generic processing element (e.g. a process unit or a path or a tree or a whole biorefinery system). This correspondence clarifies the basis for the systematisation of a combined economic value and environmental impact analysis that is a function of the process operation variables and of externalities such as feedstock and product market prices and embodied EI.

The economic cost of a material or energy carrier refers to the cost of producing one unit of the mass or energy carrier. There is an EI cost incurred from its production known as the “embodied” EI. The adoption of a life cycle approach to determine embodied EI allows the analysis to be carried out in a systematic and holistic way as required for biorefinery systems. The aggregated results from any of the various EI categories (climate change, acidification, eutrophication, human toxicity, etc.) can be used as indicators according to the goal set for the EVEI analysis. Greenhouse gas (GHG) emissions accounted for climate change category (as CO₂-eq) is used as the main environmental performance indicator due to its relevance to biofuels which face stricter policies imposed in several countries in order to be considered as sustainable (European Union, 2009). Thus, the marginal savings in GHG emissions from the biorefinery products works as an accepted and practical sustainability indicator. This saving may be certified and traded by the biorefinery in the carbon credit stock market. For consistency, the functional units for economic and EI variables are 1 kg of material streams or 1 MJ of energy streams under consideration.

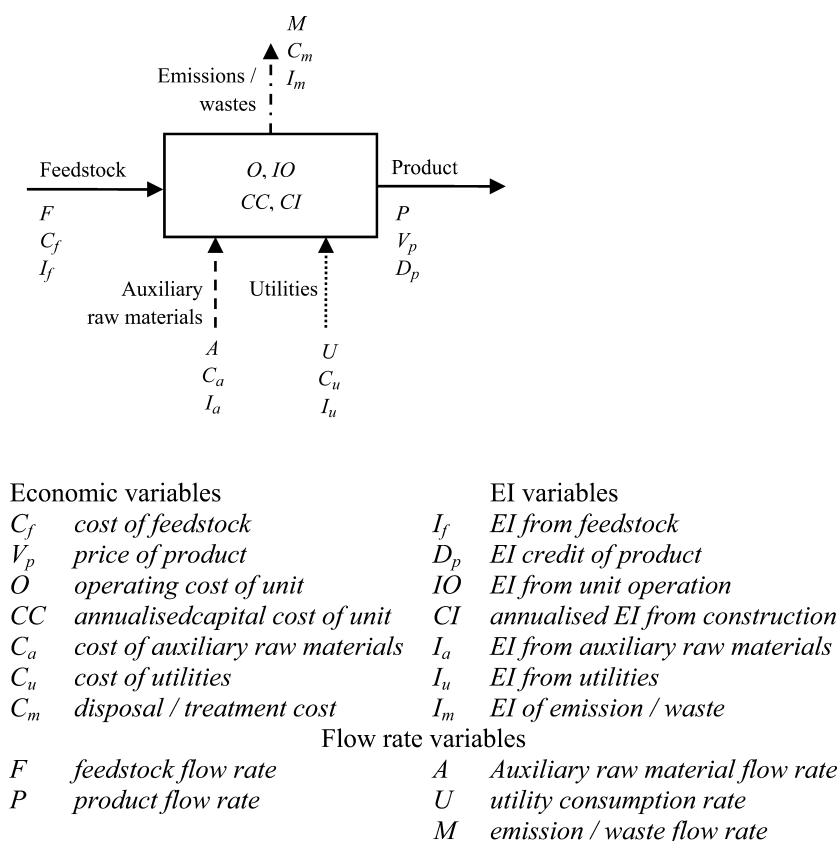


Fig. 1 – Equivalency between the economic and EI variables used in the EVEI analysis methodology.

Due to variability in biomass resources and production systems, a typical embodied factor might not represent the actual EI cost of a feedstock (I_f). To determine I_f , it is recommended to include the feedstock production within the system boundary and integrate it to the modelling. In this way, important factors affecting biomass yield and properties (e.g. nitrogen fertilisation, rainfall) can be included to track their impact on I_f and the overall results. The selection of boundaries is of high relevance to determine EI cost of biomass feedstock and EI credit value of products. Depending on the boundary, the EI cost of the biomass feedstock or EI credit value of a biorefinery product may be composed by several factors. Ideally, the system must be analysed using a cradle-to-grave approach. When using such an approach, I_f is made up of CO₂ binding from photosynthesis (B_f), EI from transportation (T_f) and EI from production (G_f) as in Eq. (2).

$$I_f = G_f + T_f - B_f \quad (2)$$

The concepts of EI cost of auxiliary raw materials (I_a) and utilities (I_u) are used to express their embodied environmental impact from production, which can be derived from the embodied impacts reported in LCA databases such as SimaPro®, Gabi®, Ecoinvent®, etc. (Rice et al., 1997; Frischknecht and Rebitzer, 2005). When produced on-site, the EI cost can be calculated from the system models. The EI cost estimation should be dynamic and determined in spatial and temporal domains. A differentiation between marketable products and emission/waste streams should be done as the latter type of stream needs to be treated, incinerated or sent to landfill and thus adds to the emission impact cost (I_m). The emission impact cost, I_m , of an emission/waste stream is calculated from its composition and components'

characterisation factors under the EI category being evaluated, or from EI generated during treatment or disposal. Similarly, the payment for emissions control and treatment or disposal of waste streams adds to a corresponding emission economic cost (C_m). Then, these costs must be allocated amongst the main process streams and then to the end products, as shown later.

The operating costs (O) of a process unit consist of the costs of utilities, and the disposal or treatment cost of any emission/waste stream produced. The impact of emissions or wastes (I_m) is taken into account in the operating impact cost (IO). In addition, an annualised capital cost (CC) using the discounted cash flow calculation over a biorefinery plant lifetime can be included in O (Sadhukhan et al., 2008). The impact from the construction materials is estimated from the preliminary equipment sizing and can be linearly distributed over the biorefinery lifetime and included in IO as an annualised EI cost of construction (CI). With the variables defined above, it is possible to make a vector representation of the total unit costs for a process unit k as in Eq. (3).

$$\bar{O}_k(X) = \begin{bmatrix} O_k \\ IO_k \end{bmatrix} = \begin{bmatrix} \bar{C}_{a,k} \\ \bar{I}_{a,k} \end{bmatrix} \times \bar{A}_k + \begin{bmatrix} \bar{C}_{u,k} \\ \bar{I}_{u,k} \end{bmatrix} \times \bar{U}_k + \begin{bmatrix} \bar{C}_{m,k} \\ \bar{I}_{m,k} \end{bmatrix} \times \bar{M}_k + \begin{bmatrix} CC_k \\ CI_k \end{bmatrix} \quad (3)$$

$\bar{O}_k(X)$ denotes unit costs as function of process variables (X). \bar{A}_k , \bar{U}_k and \bar{M}_k represent a one column vector with the flow rates of auxiliary raw materials, utilities and emissions/wastes, respectively. $\bar{C}_{a,k}$, $\bar{C}_{u,k}$ and $\bar{C}_{m,k}$ represent a one row vector containing the corresponding economic costs

whilst $\bar{I}_{a,k}$, $\bar{I}_{u,k}$ and $\bar{I}_{m,k}$ comprise a one row vector containing the respective EI costs. The inclusion of the costs from emissions and auxiliary raw materials into the total unit costs allows their allocation among the main process streams and propagation towards the end products.

3. Modelling of streams

The economic and environmental variables are correlated to the mass and energy balance analysis obtained and thereby to the process design variables. Thus, the process design variables are linked to the economic and environmental impact modelling of a stream or a unit and an entire process network. The economic and EI properties for process streams are represented by their value on processing (VOP), impact credit value on processing (CVP), cost of production (COP) and impact cost of production (ICP). The modelling of the streams starts with the known values for feedstock costs and product values. For a biorefinery product, $VOP = V_p$ and $CVP = D_p$. For a feedstock, $COP = C_f$ and $ICP = I_f$. After the establishment of these equivalencies, it is possible to generalise the modelling of economic and EI costs and values.

Consider \bar{V} as a vector containing the “values” (VOP and CVP) of a feed f to a process unit k . The vector \bar{V} can be calculated from the known values of the product streams p and the total unit costs $\bar{O}_k(X)$ through Eq. (4), where q is the number of products (excluding emissions/wastes) and g is the number of feedstock considered as main material streams (excluding auxiliary raw materials). F_f denotes flow rate of feedstocks to the unit and P_p denotes flow rate of products from the unit.

$$\bar{V}_f = \frac{[\sum_{p=1}^q \bar{V}_p P_p - \bar{O}_k(x)]}{\sum_{f=1}^g F_f} \quad (4)$$

To determine the costs of streams (COP and ICP) the cost of the process units must be allocated amongst their outlet or product streams. Allocation of impacts at a global system level is common practice in LCA. However, the evaluation of allocation factors at intermediate levels in the method presented here decreases the complexity of the allocation problem. Rather than allocating impacts to all the end products in a system, at an elementary level (unit operation) the number of products is commonly reduced to two (flash) or three (tri-phase separator). This also avoids allocating impacts to products from certain unit operations from which they are not derived at all (e.g. ethanol in a bioethanol plant is not derived from the rotary dryer used to process DDGS). Therefore, in this method the economic and EI costs from the unit operations that are used for recovery, refining or conditioning of a particular product (e.g. bioethanol purification, DDGS drying) are attributed exclusively to that product. By implementing this differentiation, the environmental impact values calculated from this method more closely reflect what is happening in the system and can provide more useful insights.

Any of the allocation methods such as mass or energy allocation and system expansion (Heijungs and Frischknecht, 1998; Azapagic and Clift, 1999c; Kim and Dale, 2002; Dalgaard et al., 2008) can be used in EVEI analysis. However, allocation by economic value at process unit level is adopted for consistency and practical reasons. The economic value is regarded as a good indicator for impact allocation since it reflects the worth of a product in a real economy. Another reason is that the VOP of intermediate streams can be readily calculated to capture

market variability. Furthermore, the resulting allocation factor (α) is a direct function of process models. This feature allows capturing the interactions at the different system levels. The allocation factor of a product stream (α_p) from a multiproduct unit is determined by using Eq. (5).

$$\alpha_p = \frac{VOP_p P_p}{\sum_{p=1}^q VOP_p P_p} \quad (5)$$

Consider now \bar{C} as a vector containing the “costs” (COP and ICP) of a product p from a process unit k . \bar{C} can be predicted for a product stream p from the known costs of the feed streams f and the total unit costs $\bar{O}_k(X)$ through Eq. (6).

$$\bar{C}_p = \frac{[\sum_{f=1}^g \bar{C}_f F_f + \bar{O}_k(x)] \alpha_p}{P_p} \quad (6)$$

The difference between \bar{V} and \bar{C} of a stream provides the margins (Δ) that indicate its potential economic profit ($\Delta e = VOP - COP$) and environmental impact saving ($\Delta i = CVP - ICP$) from production. The costs and values of the streams plotted against their mass flow rates is a graphical representation of the stream economic profile and the stream environmental profile as shown in Fig. 2. Two generic streams (S1 and S2) are presented in this figure for illustration purposes. In the stream economic profile, the area enclosed between VOP and COP is equal to the economic margin Δe multiplied by the stream flow rate and represents the total profit from the stream production. The condition for a stream to be profitable is that the VOP line is above the COP line, i.e. $VOP > COP$ (Sadhukhan et al., 2003, 2004, 2008). This results in a positive area as shown for stream S1 in Fig. 2a. A non-profitable stream would produce an economic profile similar to stream S2.

Analogously, in the stream environmental profile, the area enclosed between CVP and ICP is equal to the EI savings margin Δi multiplied by the stream flow rate and represents the total EI savings from the stream production. The condition for a stream to be sustainable is that the CVP line is above the ICP line, i.e. $CVP > ICP$, the impact credit value on (further) processing is greater than the “impact cost” of production so far. This is illustrated for stream S2 in Fig. 2b. A stream is non-sustainable when the opposite occurs, as shown in the environmental profile for stream S1. Notice that the streams used for illustration exemplify two extreme cases where a stream is profitable but non-sustainable and vice versa. Thus, the trade-offs can be easily recognised from the stream profiles.

The environmental and economic performance of a biorefinery can be evaluated from the marketable product streams. The margins of the biorefinery products contain the value generated throughout their production pathways in the process network minus the cumulative and allocated costs incurred during production. Thus, the sum of the product margins provides the total margins of a biorefinery as shown in Eqs. (7) and (8), where n is the number of biorefinery products and P_{bp} the mass flow rate of the biorefinery product bp . For instance, this sum is also equal to the total margins obtained from the feedstocks since their values result from the values of their corresponding end products minus the costs incurred by their processing. This fact indicates that the variability in market prices and in biomass properties and the interactions between the different processing elements (process units, paths and

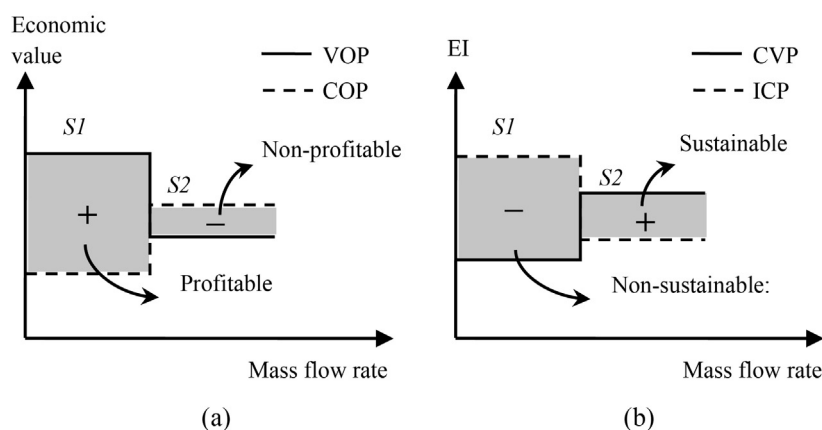


Fig. 2 – Economic (a) and environmental (b) profiles for generic streams S1 and S2.

trees) are as readily captured within the product margins as in the biomass feedstock margin, providing robustness to the EVEI analysis methodology.

$$\text{Biorefinery economic margin} = \sum_{bp=1}^n (\Delta e)_{bp} P_{bp} \quad (7)$$

$$\text{Biorefinery EI saving margin} = \sum_{bp=1}^n (\Delta i)_{bp} P_{bp} \quad (8)$$

The modelling of the streams to determine the biorefinery margins can also be helpful when comparing pathway alternatives. When two or more alternatives for the processing of a stream are evaluated (e.g. vegetable oil for biodiesel or green diesel) the trade-offs between their performance indicators (Δe and Δi) can be easily recognised. This alternative screening feature of the EVEI analysis method can be exploited to select processing routes that provide biorefinery profitability without compromising the environment, leading to a sustainable biorefinery design. Another utility of the stream margins concept is that the relative percentage of EI saving (s_p) of a biorefinery product with respect to a fossil-based product can be easily calculated using Eq. (9). This is particularly useful when evaluating the GHG emissions from the life cycle of bio-fuel production, as shown later in the case study.

$$s_p = \frac{(\Delta i)_p}{(I_{peq} \times \beta)_p} \times 100 \quad (9)$$

Once the fundamentals of the EVEI analysis have been established, the algorithms presented above can be used for the modelling of process paths, trees and entire biorefinery processing networks. Strategic methodologies can be developed depending on the objective of the analysis, e.g. new process design, process integration, biorefinery expansion or optimisation.

4. Case study

A biorefinery based in the UK producing bioethanol and DDGS from wheat grain is represented in Fig. 3. The biorefinery system is analysed using the EVEI analysis methodology to determine the sustainability of bioethanol fuel production according to the target for GHG emissions savings set by the EU directive (European Union, 2009). Thus, the EI variables of the

streams are determined as amount of CO₂ equivalents (CO₂-eq) per unit of mass (i.e. in kg kg⁻¹). Capital costs and EI from construction and transportation were not considered in this case study. The calculation basis is a biorefinery processing 1200 kt year⁻¹ (1 kt = 1 × 10⁶ kg) of wheat. Modelling of wheat production and the bioethanol process as well as economic and EI data have been adopted from Williams et al. (2006) and Sadhukhan et al. (2008).

A cradle-to-grave approach is considered to determine EI cost of feedstock and credit value of products. The allocated EI cost of wheat production from LCA modelling under UK conditions was 0.492 kg kg⁻¹ whilst the CO₂ binding corresponding to grain (excluding the straw fraction being harvested) has been reported as 1.1 kg kg⁻¹ (Küsters, 2009). Using Eq. (2) and neglecting EI from transportation, the EI cost of feedstock is

$$I_{f1} = 0.492 - 1.1 = -0.61 \text{ kg kg}^{-1}.$$

The credit values of products are calculated for $p1$ = bioethanol and $p2$ = DDGS. Since bioethanol (HV = 26.7 MJ kg⁻¹) is a biofuel substitute for gasoline (HV = 44.5 MJ kg⁻¹, $I_{peq} = 3.8 \text{ kg kg}^{-1}$), the equivalency ratio assuming the same fuel efficiency is

$$\beta = \frac{26.7}{44.5} = 0.6 \text{ kg kg}^{-1}.$$

Considering that CO₂ (molecular weight MW = 44.01 kg kmol⁻¹) is the only GHG emitted from the combustion of ethanol (MW = 46.07 kg kmol⁻¹) and that 2 mol of CO₂ are generated per 1 mol of ethanol, the EI credit value is determined using Eq. (1) as

$$D_{p1} = 3.8 \times 0.6 - 2 \times 44.01/46.07 = 0.33 \text{ kg kg}^{-1}.$$

Assuming that 1 kg of DDGS is equivalent to 0.8 kg of soy meal according to protein content comparisons (Dalgaard et al., 2008) the equivalency ratio for DDGS is thus $\beta = 0.8 \text{ kg kg}^{-1}$. Using the EI cost of soy meal of 0.726 kg kg⁻¹ (Kim and Dale, 2002), the EI credit value of DDGS is

$$D_{p2} = 0.8 \times 0.726 = 0.581 \text{ kg kg}^{-1}.$$

The costs for each process unit are summarised in Table 1. The liquefaction (LIQ-1) and the ethanol recovery units are the main contributors to economic costs with 56.7% and 17.2% of the total, respectively. 60% of the total economic operating costs come from auxiliary raw materials and 40% from utilities. Regarding EI costs, the fermentation and ethanol recovery units are the main hot spots contributing 65.5% and 14.0% of the total, respectively. In this case, the total EI costs come from

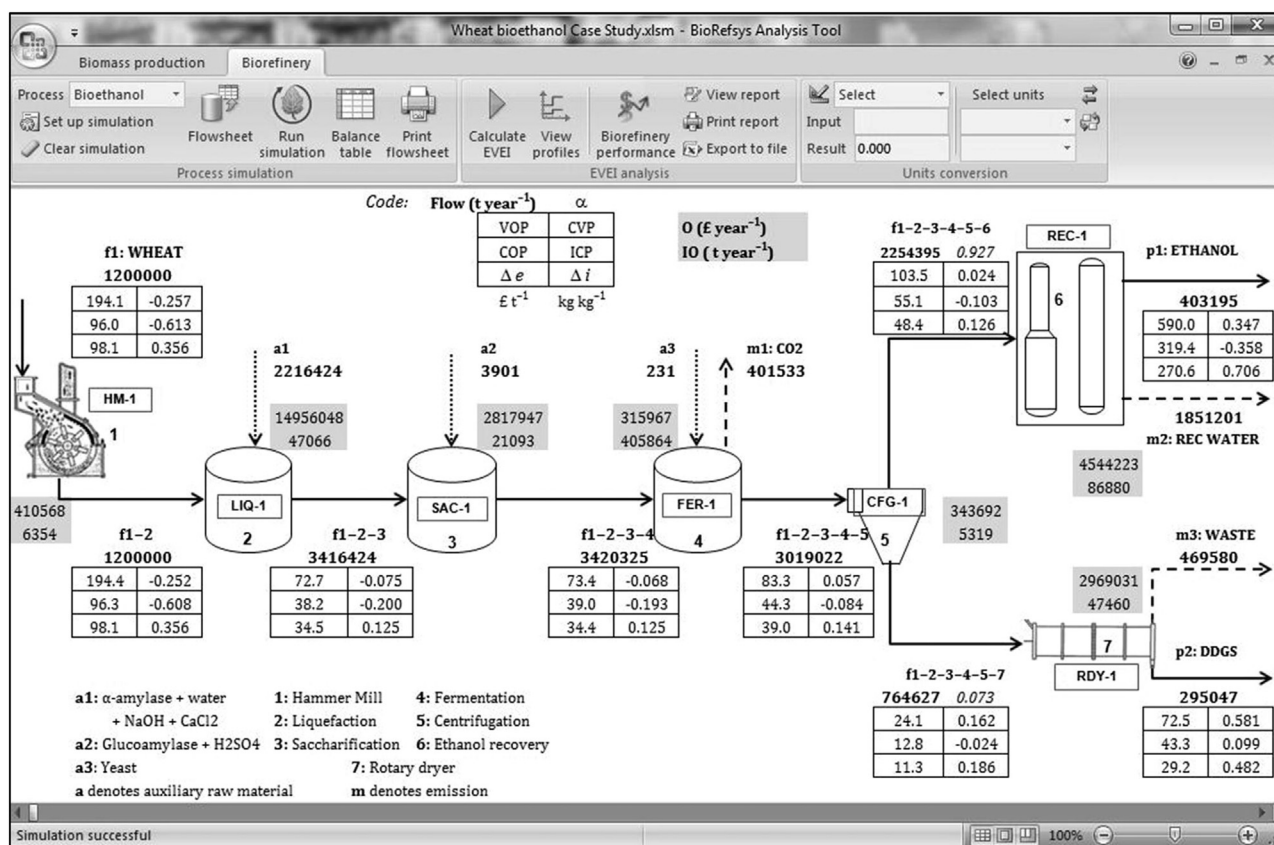


Fig. 3 – EVEI analysis results of a wheat-based biorefinery presenting mass flow rates, allocation factors (α), value on processing (VOP), cost of production (COP), economic margin (Δe), EI credit value on processing (CVP), impact cost of production (ICP) and EI savings margin (Δi) of the streams along with economic operation costs (O) and EI from operation (IO) of the units.

the emissions released during fermentation (64.8%), utilities (30.1%) and auxiliary raw materials (5.1%).

By using the unit costs from Table 1 and data for feedstock and products calculated above, the EVEI calculations can be performed. Table 2 presents the EVEI calculations for the streams around the units CFG-1 and REC-1 (Fig. 3). Notice that calculation starts with the prediction of \dot{V} through a backward calculation procedure, while \dot{C} is predicted following a forward calculation procedure. This is similar to the way that critical paths are calculated in critical path planning. This is also the natural sequence since VOP of product streams must

be known in advance to determine the EI allocation factor α . The allocation factors were found to be 0.9268 for the stream going to the bioethanol recovery and 0.0732 for the stream going to the rotary dryer.

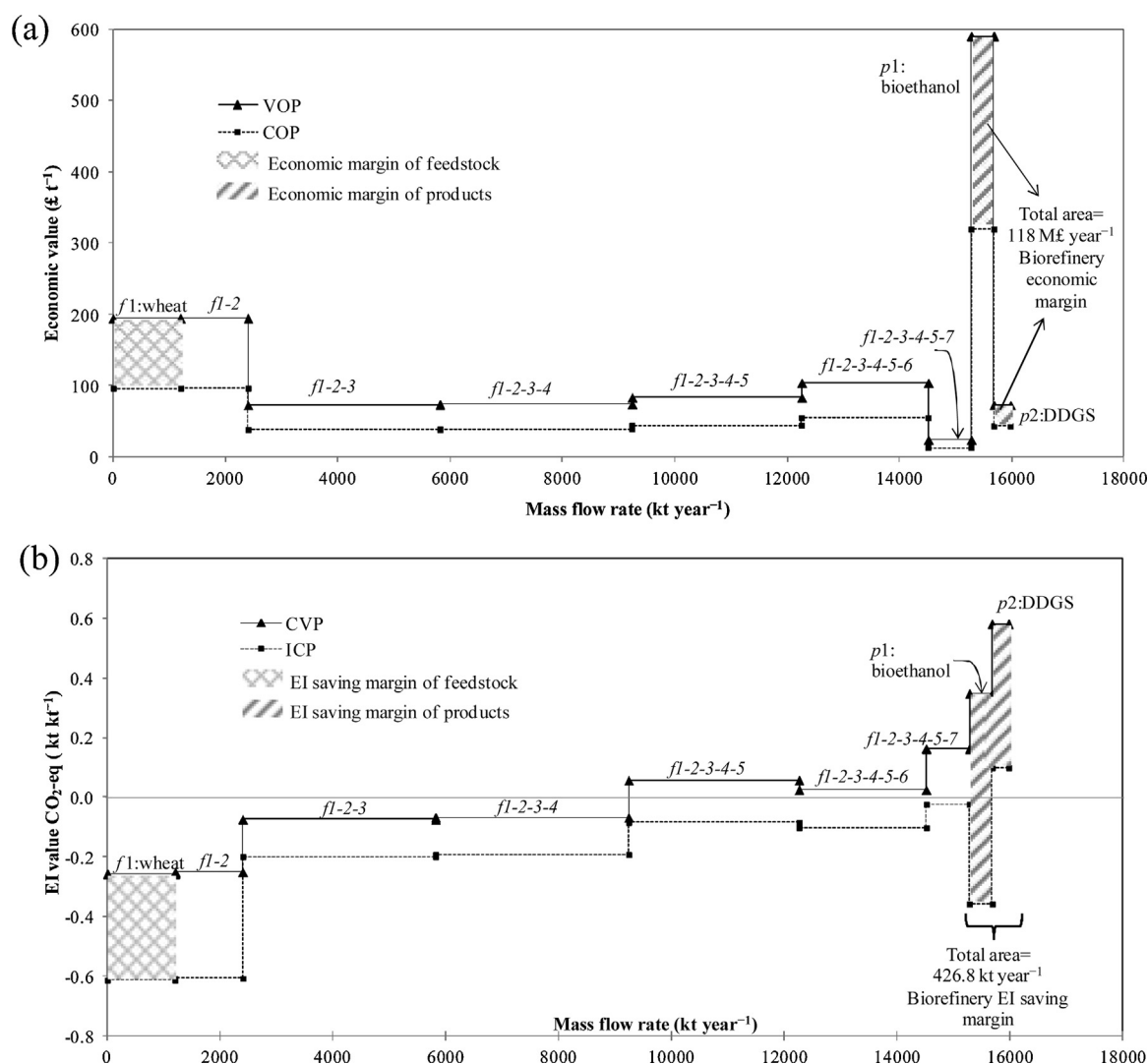
The systematisation of the methodology allowed its integration into a computer-aided process engineering (CAPE) tool developed for this purpose. The software tool includes LCA modelling for feedstock production, biorefinery process simulation and EVEI analysis calculations. All the models and calculations are programmed in VBA using an object oriented approach and use spreadsheets as a user interface. The linear

Table 1 – Economic (£ year⁻¹) and EI (t year⁻¹ of CO₂-eq) operating costs of the process units from the biorefinery in Fig. 3.

Unit	Costs	Utilities	Auxiliary raw materials	Emissions/wastes	Total
1. HM	O IO	410,568 6354			410,568 6354
2. LIQ	O IO	1,876,048 37,749	13,080,000 9317		14,956,048 47,066
3. SAC	O IO	74,719 477	2,743,228 20,616		2,817,947 21,093
4. FER	O IO	314,811 2551	1156 1780		315,967 405,864
5. CFG	O IO	343,692 5319		401,533	343,692 5319
6. REC	O IO	4,544,223 86,880			4,544,223 86,880
7. RDY	O IO	2,969,031 47,460			2,969,031 47,460
Total	O IO	10,533,093 186,790	15,824,384 31,713	401,533	26,357,476 620,037

Table 2 – Examples of EVEI analysis calculations.

Unit	Calculation
6. REC-1	<p>Values of feed:</p> $\tilde{V}_{f1-2-3-4-5-6} = [\tilde{V}_{p1}P_{p1} - \tilde{O}_6(X)]/F_{f1-2-3-4-5-6} = \begin{bmatrix} 590 \\ 0.347 \end{bmatrix} 403,195 - \begin{bmatrix} 4,544,223 \\ 86,880 \end{bmatrix} / 2,254,395 = \begin{bmatrix} 103.5 \text{ £ t}^{-1} \\ 0.02 \text{ kg kg}^{-1} \end{bmatrix}$ <p>Costs of product:</p> $\tilde{C}_{p1} = [\tilde{C}_{f1-2-3-4-5-6}F_{f1-2-3-4-5-6} + \tilde{O}_6(X)]/P_{p1} = \begin{bmatrix} 55.1 \\ -0.103 \end{bmatrix} 2,254,395 + \begin{bmatrix} 4,544,223 \\ 86,880 \end{bmatrix} / 403,195 = \begin{bmatrix} 319.4 \text{ £ t}^{-1} \\ -0.358 \text{ kg kg}^{-1} \end{bmatrix}$
5: CFG-1	<p>Values of feed:</p> $\tilde{V}_{f1-2-3-4-5} = [\tilde{V}_{f1-2-3-4-5-6}P_{f1-2-3-4-5-6} + \tilde{V}_{f1-2-3-4-5-7}P_{f1-2-3-4-5-7} - \tilde{O}_5(X)]/F_{f1-2-3-4-5} = \begin{bmatrix} 103.5 \\ 0.024 \end{bmatrix} 2,254,395 + \begin{bmatrix} 24.1 \\ 0.162 \end{bmatrix} 764,627 - \begin{bmatrix} 343,692 \\ 5319 \end{bmatrix} / 3,019,022 = \begin{bmatrix} 83.3 \text{ £ t}^{-1} \\ 0.057 \text{ kg kg}^{-1} \end{bmatrix}$ <p>Costs of products:</p> $\tilde{C}_{f1-2-3-4-5-6} = [\tilde{C}_{f1-2-3-4-5}F_{f1-2-3-4-5} + \tilde{O}_5(X)]\alpha_{f1-2-3-4-5-6}/P_{f1-2-3-4-5-6} = \begin{bmatrix} 44.3 \\ -0.084 \end{bmatrix} 3,019,022 + \begin{bmatrix} 343,692 \\ 5319 \end{bmatrix} 0.927 / 2,254,395 = \begin{bmatrix} 55.1 \text{ £ t}^{-1} \\ -0.103 \text{ kg kg}^{-1} \end{bmatrix}$ $\tilde{C}_{f1-2-3-4-5-7} = [\tilde{C}_{f1-2-3-4-5}F_{f1-2-3-4-5} + \tilde{O}_5(X)]\alpha_{f1-2-3-4-5-7}/P_{f1-2-3-4-5-7} = \begin{bmatrix} 44.3 \\ -0.084 \end{bmatrix} 3,019,022 + \begin{bmatrix} 343,692 \\ 5319 \end{bmatrix} 0.073 / 764,627 = \begin{bmatrix} 12.8 \text{ £ t}^{-1} \\ -0.024 \text{ kg kg}^{-1} \end{bmatrix}$

**Fig. 4 – Economic (a) and environmental (b) profiles of the wheat-based biorefinery system producing bioethanol and DDGS.**

process models are simulated for mass balance and energy requirement estimations which have to be input for the EVEI analysis. Mass balance is carried out in the programme. Energy requirements by individual process units and overall external energy demands (if any) are predicted. The integrated tool was used to calculate all the EVEI variables for the streams in the biorefinery. Fig. 3 is a screenshot of the software showing the biorefinery flowsheet along with mass balance, operating costs and EI of the process units and the VOP, COP, Δe , CVP, ICP and Δi of the main process streams. These values are used for further analysis as explained below.

Fig. 4 shows the economic and EI profiles for all streams in the biorefinery case study. By plotting all the main process streams in a path or tree, the evolution of the costs, values and margins throughout the process network can be easily visualised. The area of the feedstock profile or the total area of the products indicates the corresponding economic and EI saving margins of the biorefinery. From the economic profile, it can be seen that the VOP line always remains above the COP line, indicating all main streams are profitable. Notice how a stream with low economic margin like f1-2-3-4-5-7 ($\Delta e = 11.3 \text{ £ t}^{-1}$), containing the wet solids, is converted into a stream with higher economic margin (DDGS, $\Delta e = 29.2 \text{ £ t}^{-1}$) when it is further processed in the rotary dryer (RDY-1, unit 7). The gross economic potential of the biorefinery determined from Eq. 7 or from the total areas from the product streams in Fig. 4a is 118 M£ year^{-1} .

From the environmental profile, it can be seen that the impact cost of production, ICP, remains negative for the tree with the pathway producing bioethanol because of the propagation of the negative EI cost from the biomass feedstock. In the DDGS pathway, a shift in ICP from negative to positive occurs after the stream f1-2-3-4-5-7 is processed in the rotary dryer (Fig. 3). This means that the propagated negative EI cost of feedstock has been offset by the cumulative operating costs in this pathway. On the other hand, a shift in the EI credit value on processing (CVP) from positive (stream f1-2-3-4-5) to negative (stream f1-2-3-4), is produced after the fermentation unit (Fig. 3). This means that, at this point, the EI credits gained by the biorefinery products have been offset by the operating EI costs of the fermentation and downstream units. However, Δi remains positive due to the propagation of the negative EI cost of feedstock conveyed in ICP. These insights obtained from the stream profiles provide a better picture of the environmental performance of the processing elements in a biorefinery system. The potential EI margin savings from the biorefinery products is $426.8 \text{ kt year}^{-1}$ of $\text{CO}_2\text{-eq}$. That is around 3620 t M£^{-1} of $\text{CO}_2\text{-eq}$. By considering the total operating costs plus the cost of wheat ($141.6 \text{ M£ year}^{-1}$), the operating GHG mitigation costs results in 331.7 £ t^{-1} . By using Eq. (9) and results in Fig. 3, the relative GHG emissions savings from bioethanol with respect to gasoline is 31% and from DDGS with respect to soy meal is 83%. The target according to the current EU policy for a biofuel to be sustainable is 35% GHG savings (European Union, 2009). This means that the bioethanol fuel produced in the biorefinery under study may not be approved under this policy and alternatives for system improvement must be analysed before implementation.

From the hot spots identified in the system and the surplus of EI saving from DDGS, several options are available. One option is carbon capture and storage, which would compromise economic profitability due to its high costs. Another option is the use of DDGS as fuel to produce heat for ethanol recovery. The balance between CO_2 generated from DDGS

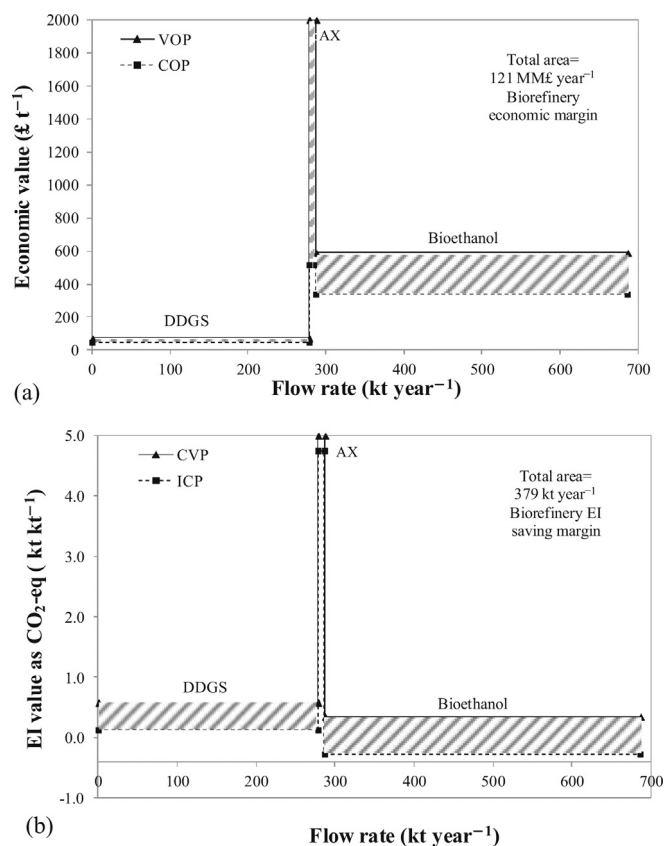


Fig. 5 – Economic (a) and environmental (b) profiles of the wheat-based biorefinery system producing bioethanol, DDGS and arabinoxylan (AX).

combustion and that saved from utilities must be positive. There is also an economic trade-off since the use of DDGS as fuel would imply fewer revenues from its production. The EVEI analysis would allow evaluation of the trade-offs that appear in every alternative and select the best option in a systematic, insightful way.

A process for the co-production of arabinoxylan (AX) from wheat bran was proposed for enhanced economics of the biorefinery (Sadhukhan et al., 2008). The process uses ethanol extraction and a series of treatment and washing steps using water, ethanol, alcalase, H_2O_2 , NaOH and H_2SO_4 . A process flowsheet can be found in Sadhukhan et al. (2008). The EVEI analysis calculation was performed for the process co-producing AX with 70% purity and using the same basis of $1200 \text{ kt year}^{-1}$ of wheat, as before. The results are presented in Fig. 5 only for the product streams. It can be observed that although it is possible to increase the economic potential of the biorefinery from 118 to 121 M£ year^{-1} (2.5% increase), the AX production process also increases the GHG emissions, thus reducing the biorefinery savings from 426.8 to $379.0 \text{ kt year}^{-1}$ (11% decrease). As a result, the saving margin from bioethanol is reduced from 0.706 to 0.628 kg kg^{-1} yielding 27.5% saving with respect to gasoline which is lower than in the biorefinery without co-production (31%). The savings of DDGS with respect to soy meal are also reduced from 83% to 78%. The increase in GHG emissions in the AX production process is mainly contributed by the chemicals used and the energy required to dry the AX product and in the various treatment steps. The GHG savings depend also on the product that AX replaces or substitutes, which at the same time will change the AX price and allocation factors of the streams. AX can be used for polymer film and as food additive. EI credit value (as

CO₂-eq) of 5.0 kg kg⁻¹ (which is within the range for polysaccharide materials reported in Shen and Patel, 2008) and equivalency ratio $\beta = 1$ have been assumed for AX.

The results suggest that a careful analysis must be done to evaluate the trade-offs between economics and environmental impact and that strategies for emissions reduction and rebalancing the GHG fluxes amongst the biorefinery products are required.

5. Conclusions

The EVEI analysis methodology proved to be useful in providing insights into the economic and environmental performance of biorefinery systems. The analogies between economic and EI concepts allow the robust manipulation of both sets of variables. The economic and EI models can be integrated into process models, throwing light on the issues of non-linearity of the production function and allocation problem not addressed by the common EI analysis methods. The systematisation allowed the implementation of the methodology as a CAPE tool in Excel-VBA platform for easy deployment, available at <http://biorefinerydesign.webs.com>.

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Chapter 6

EVEI analysis for policy compliance

6.1 Preamble

In the EVEI analysis methodology presented in Chapter 5, the *EI cost* can be the aggregated environmental impact under any of the various categories, or a normalized, weighted index. For example, the EI cost of a feedstock can be represented by the total global warming impact of GHG (as CO₂-eq in kg kg⁻¹). This is especially relevant to biofuels which face stiffer policies imposed in several countries in order to be considered as sustainable. Current policies establish targets for a minimum GHG emission saving from biofuels with respect to fossil fuels such as the EU Renewable Energy Directive (European Union, 2009) or the US Energy and Independence Security Act of 2007 (US Congress 2007). Similar policies are likely to be applied for other biorefinery products and adopted in other countries.

Figure 6.1 shows a comparison of typical GHG emissions of various biofuels and an average value for fossil fuels. The savings in relation to GHG emissions of fossil fuels are also shown along with lines indicating the different EU policy targets. The figure reveals that some biofuels, like bioethanol from wheat and biodiesel from palm oil, might not be able to meet either current or future targets. Notice that the processing stage contribution is high in most cases. This indicates a need for improvement to the biorefinery performance concerning GHG emissions from processing, especially from utilities and auxiliary raw materials.

The fact that the calculation of EI margin in EVEI analysis relates to the substitution of products based on fossil resources by the biorefinery products based on biomass resources offers the opportunity to assess the performance of a biorefinery system with respect to existing environmental policies. This feature is

exploited in the publication presented in this chapter for the compliance of future policy targets in a case study for biodiesel produced from *Jatropha* oil.

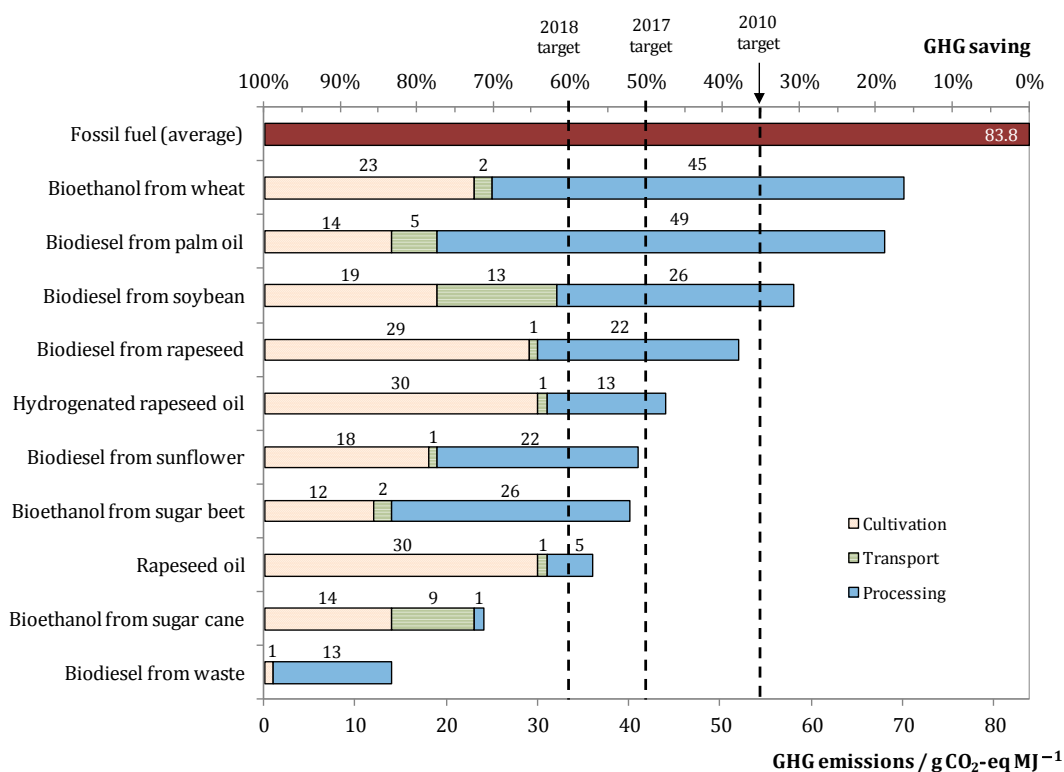


Figure 6.1 Typical GHG emissions and savings for biofuels in the EU. The dashed lines indicate policy targets for the years indicated. Adapted from UFOP (2010)

6.2 Discussion of publication 5

One of the objectives of the publication presented in this chapter is to reinforce the fundamental concepts of the EVEI analysis methodology by illustrating once again, in a different context, the calculation procedures. The more novel objective is to demonstrate how environmental policy targets could be used to guide and drive improvements in process performance and encourage waste utilisation for utility provision in order to meet policy targets. The standalone biodiesel plant previously studied in Chapter 4 is used as the case study for these purposes. This paper has been submitted to the Chemical Engineering Journal.

To ensure that policy targets for biorefinery products can be met through cost-effective process modifications, an EVEI product profile is presented in this

publication. The profile consists on a *costs composite curve* for the aggregated EI plotted against the economic costs, a horizontal *value line* indicating the EI credit value and revenue from the product, and the *limiting line* indicating the maximum allowable EI for policy target. The profile allows the visualisation of the current EI savings margin and to what extent there is a deficit or an excess of savings to meet the policy target. The representation of EI against economic values also allows identification of any trade-off resulting from a process modification which helps to select those alternatives that offer less compromise between economic and environmental performances, or those that could potentially improve both environmental and economic margins. To show this, the utilisation of waste or by-product streams for heat utility provision is explored in the case study. As a guideline, the available streams are ranked in descending order of economic margin to ensure that the improvement in EI saving is made at the lower economic loss (or cost).

The additional methodology feature provides a graphical tool to understand the effect of process integration on the EVEI analysis results and also how the consideration of policy from the biorefinery design stage can drive decision making towards more sustainable processes. However, in order to avoid that established economic and policy constraints prevent biorefineries from emerging as a new technological regime, it is crucial to have policy frameworks that are conducive to both technology improvements and commercialisation. In this respect, quantitative results from the EVEI analysis methodology as presented in this publication could be used to provide the foundations for sound policy advice.

Publication 5: Martinez-Hernandez, E., Campbell, G.M., Sadhukhan, J., 2013 *Economic and environmental impact marginal analyses of biorefineries for policy compliance*. Submitted to Chemical Engineering Journal.

costs and values as well as deficits and surpluses in EI savings. Process integration of by-products for utility generation helped to achieve GHG emission saving by 53% for biodiesel production with reference to petro-diesel, compared to 32% in the base case system. The saving was 57% for glycerol and cake and 93% for husk production in the integrated biorefinery system.

Keywords: biorefinery process optimisation, value analysis, environmental impact assessment, policy analysis, LCA

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1 Introduction

The challenge that emerges while selecting a biorefinery configuration is to find the appropriate processing pathways and products from a feedstock to ensure profitability and minimum environmental impact whilst meeting reduction targets set by policy makers. At the least, a biorefinery producing equivalent products, fuels, chemicals and combined heat and power (CHP), must clearly show economic and environmental added value over a fossil-based reference system. This requires of careful assessment of performances since the early stages of process design [1], [2].

As biorefinery configurations become more complex with new process and product developments, integrating process design and sustainability objectives will become very challenging [1]–[5]. Though previous research has taken into account the emission rates of GHG, volatile organic compounds and other substances [1]–[3], cumulative energy consumption [6], water consumption [7], biorefinery techno-economics [8]–[11] and many others ranging from energy efficiency [12] to social

49 and corporate level criteria [13], no work has so far been published on the conceptual
50 graphical analysis on combined effects for more informed decision analysis.
51 Motivated by process integration [1], [14]–[20], if such tools can be developed, these
52 will assist process synthesis, integration and optimisation tasks to generate more
53 sustainable biorefinery process configurations. There is an imperative need for multi-
54 level strategies for integrating differential marginal impacts from process streams to
55 whole systems such that policies can directly influence process design and
56 integration and vice versa. Such strategies will allow the life cycle economic and
57 environmental impact (EI) assessment to be done in a systematic manner from the
58 smallest element in a biorefinery process network (e.g. material streams and unit
59 operations, to cradle-to-grave systems). The approach must also allow identification
60 and prioritisation of pathways for process integration and optimisation that can be
61 linked with the policy targets. The whole approach can be made conceptual and
62 transparent with the help of graphical analysis.

63 To help decision makers to understand the relative merits of biorefinery systems, it
64 may mean representing the economic and environmental impact reduction targets in
65 an even more transparent and accessible way. To this end, a combined Economic
66 Value and Environmental Impact (EVEI) analysis methodology has been
67 presented [21]. The tool adapts the graphical differential network analysis approach
68 used in value analysis [22] for combined economic and environmental impact
69 analysis. In this paper, the methodology is further developed to show its value for the
70 analysis of biorefinery process design and retrofit for environmental policy
71 compliance. This is demonstrated by analysing a biorefinery system with *Jatropha*
72 *curcas* seeds as feedstock and using the methodology to improve the system in order
73 to meet GHG emission reduction targets.

74 **2 Methodology**

75 **2.1 Concepts of EVEI analysis**

76 The value analysis tool has been developed for differential economic
77 marginal analysis from process streams to networks [22]. It enables evaluation and
78 graphical presentation of a network margin in terms of the cost of production (COP),
79 value on processing (VOP) and margins of individual streams in a process
80 network [22], [23]. A stream showing a negative economic margin implies that it
81 would be better (if possible) to purchase that stream from the market rather than
82 produce it within the process. The evaluation of COP starts from the known market
83 prices of feedstocks and proceeds in the forward direction until end products are
84 reached. The COP of a stream is the summation of all associated cost components
85 (i.e. the costs of feedstocks, utilities and annualised capital costs) that have
86 contributed to the production of that stream up to that point. This must mean
87 inclusion of only those fractional costs involved with the stream's production. The
88 VOP evaluation proceeds in the backward direction from the end product market
89 prices until the feedstock in a process network is reached. The VOP of a stream at a
90 point within the process is obtained from the prices of products that will ultimately
91 be produced from it, minus the costs of auxiliary raw materials and utilities and the
92 annualised capital cost of equipment that will contribute to its further processing into
93 these final products. The COP of a feedstock to a process and the VOP of an end
94 product correspond to their respective market prices.

95 Equivalent to the COP and VOP, the environmental impact (EI) cost of
96 production and EI credit from fossil-based product displacement can also be
97 evaluated stream by stream, in order to understand quantitatively the origins of

98 environmental impacts and the opportunities for reduction through modification of
99 process configurations. A stream with a positive environmental impact margin
100 (difference between EI credit and EI cost) would indicate that there are EI benefits
101 from its processing while a stream with a negative EI margin would indicate that its
102 production generates more EI than the EI credit obtained. This basic concept allows
103 the analysis of the performance of biomass-based products from a biorefinery and
104 comparison with that of a fossil-based product. A stream with a negative EI margin
105 would be better (if possible) bought in from a process that produces it with a positive
106 EI margin. When this is not possible but it has economic value, its production
107 pathway must be improved by using process integration and energy and raw
108 materials with a lower embodied EI.

109 In a cradle-to-grave life cycle approach (including biomass production system,
110 biorefinery process, transportation and end use of products) the CO₂ captured during
111 photosynthesis, direct wastes and emissions can be taken into account within the EI
112 variables of feedstock and products. The EI cost (GHG as CO₂ equivalents) of
113 feedstock I_f is made up of the CO₂ binding by photosynthesis (B_f), the EI cost from
114 transportation (T_f) and EI cost from production (G_f), shown in Eq. 1. This equation
115 shows that for a biorefinery to be environmentally feasible, B_f must be greater than
116 the EI added to the system by G_f and T_f .

$$I_f = G_f + T_f - B_f \quad (1)$$

117 In that case, I_f is negative, indicating feasibility of an overall biorefinery system
118 and that the GHG emission is reduced due to CO₂ capture during photosynthesis.
119 When the various crop fractions are utilised in a biorefinery e.g. Jatropha oil for

120 biodiesel and seed husks for combined heat and power, the CO₂ binding may need to
121 be allocated to various products.

122 The EI credit value of a biorefinery product is the net avoided emission, shown
123 in Eq. 2. The EI credit value of a biorefinery product (D_p) is made up of the emission
124 from an equivalent product being replaced (I_{peq}), multiplied by a unitless equivalency
125 factor β , minus the EI cost from end use emissions (I_{end}) and transportation (T_p). β ,
126 for example, is the ratio between the calorific value of a biofuel produced from a
127 biorefinery and that of an equivalent fossil based transportation fuel.

$$D_p = \beta \times I_{peq} - T_p - I_{end} \quad (2)$$

128 This equation shows that for a biorefinery product having environmental
129 advantage over a fossil-based counterpart, D_p must be positive. I_f represents the
130 starting point for forward EI cost calculations of streams and units within the
131 process, analogous to the purchase cost of the feedstock in value analysis, while D_p
132 represents the starting point for the backward EI credit calculations of intermediate
133 streams and units, analogous to the selling price of the product in value analysis.

134 2.2 Modelling of streams

135 Equivalent to streams' economic performance indicators, VOP and COP, their
136 EI indicators are their individual impact Credit Value on Processing (CVP) and
137 Impact Cost of Production (ICP), respectively. As noted above, for a final product,
138 $CVP = D_p$. For an initial feedstock, $ICP = I_f$.

139 *VOP and CVP of streams.* Since VOP and CVP of a biorefinery end product are
140 known from reported market prices and embodied EI of the fossil-based product
141 being replaced, respectively, the calculation proceeds backwards from the end

142 products towards the feedstock. Consider \bar{V} as a vector containing VOP and CVP of
 143 a main feed stream f to a process unit k (excluding auxiliary raw materials to avoid
 144 double accounting in Eq. 3). The vector of values can be calculated from the known
 145 vector of values of the product streams p minus the total costs \bar{O}_k of process unit k
 146 through Eq. 3:

$$\bar{V}_f = \left[\sum_{p=1}^q \bar{V}_p P_p - \bar{O}_k \right] / \sum_{f=1}^g F_f \quad (3)$$

147 P_p and F_f corresponds to the mass flow rate of product and feedstock,
 148 respectively.

149 *COP and ICP of streams.* The ICP of a stream represents the EI incurred from
 150 its production. To evaluate the ICP of a stream, the operating and construction EI
 151 costs of the process unit are added to the total ICP of the feed and divided by the
 152 product mass flow rate. The COP of a product stream is evaluated in the same way
 153 using the corresponding economic variables. \bar{C} in Eq. 4 is a vector containing the
 154 costs (COP and ICP) of a product p from a process unit k (excluding emission and
 155 waste streams to avoid double accounting in Eq. 4). \bar{C} can be predicted for a product
 156 stream p from the known vector of costs of feed streams f and total costs of process
 157 unit k :

$$\bar{C}_p = \left[\sum_{f=1}^g \bar{C}_f F_f + \bar{O}_k \right] / P_p \quad (4)$$

158 The economic operating costs (O_k) of a process unit consist of the costs of
 159 utilities, auxiliary raw materials and the disposal or treatment cost of any
 160 emission/waste stream produced. The analogous operating EI cost is indicated by

161 IO_k . The capital cost can be estimated from equipment sizing and annualised using a
 162 capital charge determined from the net present value, internal return rate and the
 163 discounted cash flow calculations [22],[23]. The total impact from construction can
 164 be also estimated from equipment sizing and the type of materials and their EI and
 165 then annualised using the life time of a facility. The annualised economic capital cost
 166 and EI costs of construction are fixed costs that can be added to the operating costs to
 167 determine the total costs of a unit as shown in Eq. 5.

$$\bar{O}_k = \begin{bmatrix} O_k \\ IO_k \end{bmatrix} = \begin{bmatrix} \bar{C}_{a,k} \\ \bar{I}_{a,k} \end{bmatrix} \times \bar{A}_k + \begin{bmatrix} \bar{C}_{u,k} \\ \bar{I}_{u,k} \end{bmatrix} \times \bar{U}_k + \begin{bmatrix} \bar{C}_{m,k} \\ \bar{I}_{m,k} \end{bmatrix} \times \bar{M}_k + \begin{bmatrix} CC_k \\ CI_k \end{bmatrix} \quad (5)$$

168 \bar{O}_k denotes total costs of a process unit as function of process variables.

169 \bar{A}_k , \bar{U}_k and \bar{M}_k represent single column vectors of mass flow rates of auxiliary
 170 raw materials, utilities and emissions/wastes, respectively.

171 $\bar{C}_{a,k}$, $\bar{C}_{u,k}$ and $\bar{C}_{m,k}$ are single row vectors containing economic costs, while
 172 $\bar{I}_{a,k}$, $\bar{I}_{u,k}$ and $\bar{I}_{m,k}$ are a one row vector containing the respective EI costs.

173 CC_k and CI_k are annualised capital cost and annualised EI from construction,
 174 respectively.

175 The inclusion of the costs from emissions and auxiliary raw materials in the total
 176 costs allows their allocations amongst process streams and propagation towards end
 177 streams in both directions. An allocation factor (α) is determined in case of multi-
 178 output process units. For a stream from single output units $\alpha=1$. Although any
 179 allocation method such as by mass, energy content or carbon content can be
 180 suited [24]–[27] for the EVEI analysis, the allocation by economic value using VOP
 181 has been adopted.

182 The difference between \bar{V} and \bar{C} of a stream provides its margins (Δ):
 183 economic, $\Delta e = \text{VOP} - \text{COP}$, and avoided emission or EI saving, $\Delta i = \text{CVP} - \text{ICP}$.
 184 When the aim is to improve the percentage GHG savings, hence addressing policy
 185 targets of biorefinery products with reference to fossil-based equivalent
 186 products [28],[29], the relative percentage of EI savings (s_p) of a product can be
 187 calculated using Eq. 6.

$$s_p = \frac{\Delta i}{(I_{peq} \times \beta)} \times 100 \quad (6)$$

188 Built upon the principles of environmentally friendly process design with the
 189 most efficient use of energy, raw materials and capital, the process integration tools
 190 help to identify a network's bottleneck and shift loads (e.g. energy / water / materials
 191 / environmental impact) from constrained to unconstrained parts for overall
 192 improved performance [30]–[33]. In order to facilitate compliance with existing
 193 legislation, it is possible to shift the environmental burden from one product to
 194 another following a process integration approach. Consideration of the network
 195 connectivity integrates process operations, economic and environmental indicators to
 196 policy drivers. The concepts and methodological procedures developed above along
 197 with the construction of an EVEI profile, presented in the next section, can be
 198 effectively used for the targeting of avoided emissions for future low carbon
 199 adaptation under a strict policy scenario.

200 **2.3 EVEI profile of a product**

201 An EVEI profile represents the cumulative economic, environmental impact
 202 costs and values and the resulting margins for a biorefinery product. This graphical

representation allows identification of the “distance to target” and quantification of any deficit or excess of EI savings in respect to a policy target and also the resulting economic or environmental compromises from any option for performance improvement. A generic EVEI profile is presented in Figure 1, featuring the following:

Figure 1

- *Costs composite curve* is a plot of cumulative EI costs versus economic costs from the feedstock, auxiliary raw materials, utilities, process emissions and fixed costs (annualised capital costs or EI cost from construction) allocated to a particular product. These costs are plotted as in the order given in a plot of EI in the y-axis and economic value (EV) in the x-axis. In Figure 3, the steeper slope of the contributions from utilities and auxiliary raw material compared with feedstock indicate higher EI contribution per \$ spent, while the very small slope of process emissions and fixed costs indicates that there is low EI contribution per \$ spent.
- *EI cost limiting line* indicates a benchmark for the EI cost target from the production of a biorefinery product established from policy. The limiting line starts at (0,0) and the end point is $(COP_p \times P_p, ICP_{p, \text{limit}} \times P_p)$. $ICP_{p, \text{limit}}$ is determined using Eq. 6 for the percentage EI saving set by the policy target ($s_{p, \text{target}}$) and the definition of $\Delta i = CVP - ICP$ as: $ICP_{\text{limit}} = CVP - (s_{p, \text{target}} \times I_{\text{peq}} \times \beta / 100)$.
- *Value line* is a horizontal line drawn from the EI-axis to the point of total EI credit value ($CVP_p \times P_p$) against the total economic value on processing

226 (VOP_p×P_p). This line indicates a reference limit to get positive economic and EI
227 saving margins.

228 • *Product EI saving surplus/deficit* is the distance from the value line to the end of
229 the limiting line indicating the EI saving margin required to meet the policy
230 target. The distance from the end point of the costs composite curve and the
231 limiting line determines the difference between the EI saving margin achieved
232 and the policy target. If the composite curve is below the limiting line, then there
233 is a surplus EI saving and then stricter policy target for GHG emission reduction
234 could be met.

235 The application of the EVEI methodology developed above and the use of
236 product EVEI profiles to analyse options for accomplishing policy targets is
237 demonstrated in a case study presented in the next section.

238 **3 Case study**

239 The Jatropha-based biorefinery configuration in Figure 3, producing 100 kt y⁻¹
240 of biodiesel and the corresponding amounts of glycerol, seed cake and husk, has been
241 selected as case study. The context is that it is located in Mexico within the radius of
242 a Jatropha plantation in the state of Michoacan. The current 50% GHG emission
243 reduction target set in US policies (as of 2012) for biofuel production [28] is the
244 reference point used in the analysis for policy compliance and applied to all the
245 products. The seeds are assumed to be produced by non-toxic Jatropha provenances
246 native to Mexico. Therefore, seed cake can be used as animal feed. The various
247 modelling approaches for each biorefinery subsystems are described as follows.

248

249 **3.1 Feedstock production**

250 The EI results for Jatropha seeds production system deduced from the
251 inventory data given in Table 1 are shown in Table 2. Since nitrogen fertilisation is a
252 hot spot in the system and an important decision variable, two different fertilisation
253 rates were studied to track the effect of reducing current fertilisation rate. It can be
254 observed that estimated yield from models correlating yield to average annual
255 rainfall and nitrogen fertilisation is not significantly affected by the reduction in
256 fertilisation rate resulting in lower EI cost of production. The feedstock production
257 model is shown in [34].

258 **Table 1**

259 **Table 2**

260 **3.2 Biorefinery process model**

261 Models for seed processing were developed in a spreadsheet, while Jatropha oil
262 conversion into biodiesel was simulated in Aspen Plus[®] [35]. The heating values of
263 Jatropha fruit fractions used for mass and energy balance calculations are shown in
264 **Table 3**. The overall mass balance of the biorefinery process is presented in Figures
265 3 and 4. The process consists of seed dehusking producing husk as a substitution fuel
266 for natural gas. The seed kernels are oil extracted wherein seed cake meal is co-
267 produced as a protein source substituting soy meal. The oil undergoes
268 transesterification with methanol using heterogeneous catalyst, which allows
269 flexibility on free fatty acid content in the feedstock and high conversion into
270 biodiesel and high purity glycerol. Methanol is recovered by distillation and recycled
271 to the transesterification reactor. Glycerol is separated by decantation and sold to the
272 market, replacing glycerol from fossil resources.

273 **Table 3**

274 The simulation flowsheet and streams' compositions and flowrates of Jatropha
275 oil conversion into biodiesel are shown in Figure 2. Oil was modelled as a mixture of
276 tryglycerides (TG) made up of triolein, tripalmitin, trilinolein and tristearin, free fatty
277 acids (FFA) was modelled as oleic acid. Properties of these components and the
278 corresponding fatty acid methyl esters (FAME) are not available in Aspen Plus
279 database. The basic properties (e.g. molecular weight, density, molecular structure)
280 were introduced and the UNIFAC-Dortmund physical property model was used for
281 predicting remaining properties. The process specifications for the simulation model
282 are presented in Table 4.

283 **Figure 2**

284 **Table 4**

285 Heat integration was carried out to minimise the utility requirements as shown in
286 Figure 2. The reaction mix stream is preheated (from 26°C to 70 °C) by the bottom
287 stream of the methanol recovery column (from 167 °C to 135 °C). The crude
288 biodiesel stream (25 °C) fed to the recovery column can also be preheated to 301 °C
289 by the distillate biodiesel stream (at 317 °C cooled to 35 °C) thus reducing reboiler
290 duty. The heat requirements after heat integration were used for the inventories. The
291 operating inventories and costs are shown in Table 5.

292 **3.3 Other assumptions**

293 From the predicted seed yield of 4213 kg/ha (Table 2) and the total seed
294 requirement of 271.2 kt/y (Figure 3), the total land use is 64385 ha/y. Thus, a
295 transportation distance of 14.3 km is obtained assuming circular shape. The same

distance is assumed for seed cake and husk being used locally. For transportation of other products and materials, the distance is assumed to be 100 km.

The EI from construction materials was estimated assuming that process equipment is made up of 70% steel and 30% aluminium. The mass of steel was estimated from the preliminary equipment sizing [36]. Distillation columns were sized using the built-in feature in Aspen Plus® for such purpose. Then, the weight of the vessels was determined using a weight calculator tool [37]. The weight of dehusking machines was estimated from vendor data. Cost of vessels, pumps and heat exchangers were estimated using the CapCost software tool [36]. Prices were levelised using the Chemical Engineering Plant Cost Index (CEPCI) reported in [38]. The cost of transesterification, decantation and distillation units in the biodiesel process includes pumps and heat exchangers around main equipment. The resulting total fixed costs (capital and EI from construction) of the units are summarised in Table 5. To annualise the economic and EI costs of the process units, the operation time of 7920 h/y, capital interest rate of 10% and plant life time of 15 years were assumed. The resulting annual capital charge ratio is 0.1315.

Table 5

4 Results and discussion

4.1 EVEI results and overall biorefinery performance

The VOP, COP and Δe from the EVEI modelling of the streams are presented in Figure 3. The biodiesel cost of production (COP) was estimated as 627.7 \$ t⁻¹ or 0.55 \$ L⁻¹ (7.44 MX\$ L⁻¹, 1 \$=13.5 MX\$) which means it has the potential to be competitive with petro-diesel prices in Mexico (10.81 MX\$ L⁻¹, August 2012). The

methanol recycle has been considered as a utility stream for units 3 and 4 considering its market price (i.e. $27.2 \times 1000 \times 372.1 = 10,121,120$ \$ y⁻¹). For unit 4 (methanol recovery), the total costs are recalculated as O₄' by subtracting the economic value of the methanol recycle. For unit 3 (transesterification), the methanol recycle presents an additional cost. Thus O₃' is calculated by adding the economic value of the methanol recycle to O₃. The total treatment cost of the oily waste is included in the total cost of the biodiesel distillation unit (number 6).

Figure 3

The calculations of EI cost of feedstock and EI credit value of the products are shown in Table 6. CO₂ emissions from the processing and end use (e.g. combustion) were considered as balanced as they originate from the carbon contained in Jatropha seeds. Within this system boundaries (from seed production to product distribution point), Eq. 1 reduces to $I_f = G_f + T_f$ while Eq. 2 reduces to $D_p = \beta \times I_{peq} - T_p$. However, the CO₂ from the carbon atoms added from fossil-based methanol to methyl esters in biodiesel was accounted (0.157 kg kg⁻¹). For seed husk, the heating value in Table 3 is used as factor to convert D_p from kg MJ⁻¹ to kg kg⁻¹.

Table 6

The CVP, ICP and Δi are shown in Figure 4. The oil extracted has an ICP (CO₂ equivalent) of 1.497 kg kg⁻¹ based on the ICP of the incoming seed kernel of 0.909 kg kg⁻¹, to which is added the fractional EI cost of the utilities and equipment construction materials using allocation factor and stream mass flow rates (i.e. $(0.909 \times 179800 + 30572) \times 0.8079 / 104700 = 1.497$ kg kg⁻¹). Similarly, working backwards from the end, the CVP of the stream entering the biodiesel distillation is 2.605 kg kg⁻¹, based on the biodiesel CVP minus the total EI costs of the unit,

343 including EI from oily waste, and the stream flow rates (i.e.
344 $(2.779 \times 100000 - 3652) / 105300$). Table 7 further exemplifies EVEI calculations.

345 **Table 7**

346 The economic and environmental impact profiles for the biorefinery marketable
347 products are shown in Figure 5a and 5b, respectively. The area between the values
348 and costs of each product represents its economic margin and potential EI saving.
349 The sum of areas represents the total biorefinery margins. The profiles show that the
350 biorefinery is profitable and that all the products provide EI savings (thus, streams
351 are sustainable according to this criterion).

352 **Figure 4**

353 **Figure 5**

354 **4.2 Policy compliance and EVEI profiles**

355 Substituting β , I_{peq} and Δi in Eq. 6, the following % EI savings of end products
356 are calculated. Biodiesel with respect to petro-diesel = 32%; Glycerol with respect to
357 fossil-based glycerol = 36% and seed cake with respect to soy meal = 31.5%. These
358 values are lower than the minimum GHG emission reduction target of 50%. Thus,
359 improvements in the biorefinery process system are required in order to meet the
360 targets for these two products. The only product that can meet the policy target is
361 seed husk (used as fuel), which achieves 90.5% savings with respect to natural gas.

362 **Figure 6**

363 Figure 6 shows the EVEI profile of biorefinery products in the base case system.
364 A composite factor (α'), determined from the product of allocation factors of the
365 outlet streams (α) from each process unit in a product path, is used to calculate the

fractional costs for a particular product as shown in Table 8. These factors are used to generate the data points in the EVEI profile of a product as shown for the economic costs allocated to biodiesel in Table 9. The data points for EI costs are determined following a similar approach. The composite factors (α') will change with any change in economic value of the streams as they determine the allocation factors α . The data points for the value and the limiting lines are determined as discussed in Section 2.3.

It can be observed that biodiesel fails to meet the policy target with a deficit in EI saving (as CO₂-eq) of 52.3 kt y⁻¹. Glycerol incurs a deficit by 5.5 kt y⁻¹ while the deficit from seed cake is 10.1 kt y⁻¹. Husk exhibits EI saving surplus of 38.5 kt y⁻¹. If the surplus savings of seed husk are shifted to make up for the deficits of biodiesel and glycerol, there is still an overall deficit of about 29 kt y⁻¹. As the values are interrelated by the EVEI models, the EI saving across the products can be more evenly distributed and improved by integration strategies. It can be also observed from Figure 6 that feedstock is one of the major sources of EI for all the products while emissions from utilities and auxiliary raw materials are also important for biodiesel and glycerol productions. Contribution of utilities is not significant for cake production, while only feedstock EI is relevant for husk EI. These results provide insights into the utilisation of waste and by-product streams for low impact utility generation.

Table 8

Table 9

388 4.3 Process integration and policy targets

389 Streams with potential as fuels for utility supply were ranked from the lowest to
390 the highest Δe in order to sequentially apply process integration strategies: oily waste
391 < husk < seed cake < glycerol. The EVEI analysis results of modifications a-d below
392 are summarised in Table 10.

- 393 a. Decrease the fertilisation rate from 162 kg ha^{-1} to 100 kg ha^{-1} (Table 2). This
394 modification increased the % saving of all the products. However, the 50% EI
395 saving target for biodiesel, glycerol and cake was not met and thus modifications
396 b and c were required.
- 397 b. The heat from oily waste stream can be recovered into steam generation for the
398 methanol and biodiesel distillation columns' reboilers. The EI saving margins
399 were increased for all the products and the policy target is only achieved for
400 glycerol (Table 10) but the modification was not enough to achieve the target for
401 biodiesel and cake.
- 402 c. Further, a portion of seed husk needs to be used for heat generation for the oil
403 extraction unit. The amount of husk required was 8.2 kt y^{-1} replacing 36.5% of
404 the heat demand by the oil extraction unit. The boiler annualised capital cost and
405 revenue losses from the use of husk can be balanced off by the economic cost
406 saving due to natural gas replacement. As shown in Table 9, all the products
407 achieved EI saving equal to or greater than 50% in relation to the corresponding
408 fossil-based product being displaced.

409 The cost of production of biodiesel was decreased from $627.7 \text{ \$ t}^{-1}$ in the
410 initial system to $621.6 \text{ \$ t}^{-1}$ after the modifications a-c. This is due to a net
411 saving of about $0.8 \text{ M\$ y}^{-1}$ from the integrated use of oily waste and husk for

412 heat generation. The net positive EI saving is 65 kt y⁻¹ (CO₂ equivalent). Thus
413 the total biorefinery margin is increased from 7.0 M\$ y⁻¹ to about 7.8 M\$ y⁻¹
414 (11% increase) and the EI savings from about 213 kt y⁻¹ to 278 kt y⁻¹ (30%
415 increase) with respect to the initial system.

416 Figure 7 shows the effect of improvements “a” to “c” in the costs composite
417 curve of all the biorefinery products. The curve for biodiesel (Figure 7a) is
418 shown displaced downwards to the limiting line indicating that policy target can
419 be met. Glycerol, cake and husk display significant surpluses. Note that the
420 value line for husk (Figure 7d) is also displaced downwards and to the left,
421 indicating the revenue loss and reduction of total EI saving due to use of husk
422 within the system. The EI saving from utility supply from husk has been shifted
423 and distributed to the other biorefinery products.

424 d. Further improvement could be realised by generating the entire heat required
425 by the oil extraction unit using husk. The effect on the performances is analysed
426 as in the case of improvement c and the final results are shown in Table 10 under
427 modification “a to d”. It can be observed that EI savings are increased for
428 biodiesel to 53% and for glycerol and cake to 57%. The total biorefinery
429 economic margin remains the same after modifications a-c. The total biorefinery
430 EI savings are 281 kt y⁻¹, 32% increase with respect to the initial system.

431 As shown in Table 10, the saving from husk relative to its fossil counterpart
432 remains the same after modifications; this is because the total EI saving from husk
433 replacing natural gas is reduced in the same proportion as the mass flow rate utilised
434 within the process as fuel. In addition, utilisation of husk does not modify
435 performance of the dehusking unit itself as most of the energy generated from husk is

436 used downstream, affecting the performances of the rest of the units and their
437 products.

438 **Figure 7**

439 **Table 10**

440 **5 Conclusions**

441 The economic value analysis results can be combined with the environmental
442 impact analysis results for more integrated process design and decision making. The
443 EI analysis has been shown using the global warming potential as a criterion.
444 However, in principle, any environmental impact characterisation can be presented in
445 the same way as the global warming potential, alongside the economic assessments.
446 The EVEI tool has proved to be useful to evaluate options for improvement of
447 biorefinery process designs from differential product EV and EI marginal analysis.
448 By using a multi-level strategy, the tool is capable to capture the effects of process
449 and market variables on the marginal values. Both empirical and fundamental
450 thermodynamic-based models can be integrated, allowing handling of non-linear
451 models in the EI allocation problems.

452 Integration strategies similar to those used in the case study can be developed for
453 a scenario where the rebalancing of EI to achieve policy targets entails an economic
454 cost – the benefit of meeting the target would then need to be balanced against the
455 economic cost. Simultaneously, total site integration tools can be applied for
456 integrated biorefinery design, since not only the EI can be reduced, but also the
457 emission reduction targets can be increased and a higher biorefinery economic
458 margin can be obtained. For stricter emission reduction policy in the future,
459 conversion of husk into methanol, heat and power for the biodiesel production

460 process can be considered. Analysis including carbon credit trading can also be used
461 to determine the investment incentives for integrated biorefinery systems.

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Table 1 Inventory data for Jatropha seed production.

Inventory	Functional unit	El cost (g CO ₂ -eq)	Amount input
N fertiliser	kg	2940	162 kg ha ⁻¹
P fertiliser	kg	1160	162 kg ha ⁻¹
K fertiliser	kg	380	162 kg ha ⁻¹
Machinery	h	2.912	2h ha ⁻¹ , 42.6 kW tractor
Diesel	MJ	74.4	6584 MJ ha ⁻¹
Electricity from grid	MJ	173.4	27.8 MJ ha ⁻¹
Storage area	m ²	4.721	3.7 m ² ha ⁻¹
Abamectin (pesticide)	L	13.12	2 L ha ⁻¹
Glyphosate (herbicide)	L	13.12	2 L ha ⁻¹

Table 2 EI (as CO₂-eq) results from the Jatropha seeds production system.

EI source	EI (kg ha ⁻¹)	EI (kg ha ⁻¹)
	162 kg ha ⁻¹ nitrogen fertilisation rate	100 kg ha ⁻¹ nitrogen fertilisation rate
Field operations	42	42
Fertilisers	872	538
Pesticides	63	63
Fruit de-shelling	33	34
Seed conditioning	423	428
Storage	17	17
Direct and indirect field emissions	1206	744
Total EI	2657	1867
Estimated seed yield (kg ha ⁻¹)	4213	4260
EI cost of production of seeds (kg kg ⁻¹)	0.631	0.438

Table 3 Fractions of Jatropha fruit and their heating values.

Fractions	FRUIT		SEED		KERNEL	
	Shell	Seed	Husk	Kernel	Oil	Cake
Mass (%)	31.0	69.0	33.7	66.3	58.2	41.8
Heating value (MJ kg ⁻¹)	17.28	27.1	19.84	30.9	39.6	18.3

Table 4 Specifications for the biodiesel process simulation in Aspen Plus.

Equipment	Aspen model	T (°C)	P (kPa)	Other specifications	
RMIXHTR	Heater	70	101.3		
TEREACT	Rstoic	70	101.3	TG conversion fraction	0.93
				FFA conversion fraction	1
MEOHREC	RadFrac		40	Pressure drop (bar)	0.1
				Stages	16
				Methanol mass recovery (%)	99
				Molar reflux ratio	2
RECPUMP	Pump		200		
COOL1	Heater	25	101.3		
DECANT	Decanter	25	101.3		
BIODREC	RadFrac		101.3	Stages	4
				FAME mass recovery (%)	99
				Molar reflux ratio	0.2
PREH1	Heater		101.3	Duty (MW)	2.27
PREH1-1	Heater	35	101.3		
COOL2	Heater	35	101.3		

Table 5 Inventories per tonne of biodiesel product and the estimated total capital cost and EI from construction of the various process units.

Process unit	Steam (MJ t ⁻¹)	Electricity (MJ t ⁻¹)	Cooling water (MJ t ⁻¹)	Hexane (kg t ⁻¹)	CaO (kg t ⁻¹)	Methanol (kg t ⁻¹)	Capital cost (\$)	EI construction (t) as CO ₂ -eq
Dehusking	–	58.6	–	–	–	–	743028	209
Oil extraction	2686.4	356.0	–	7.192	–	–	5669942	No data
Transesterification	–	–	285.1	–	15.7	11.50	442000	1437
Methanol recovery	1092.0	129.43	844.0	–	–	–	1593400	3472
Decantation	–	–	248.1	–	–	–	175300	196
Biodiesel distillation	396.32	–	376.4	–	–	–	881400	447
Cost	5.61 \$ GJ ⁻¹	25.68 \$ GJ ⁻¹	1.053 \$ GJ ⁻¹	969 \$ t ⁻¹	400 \$ t ⁻¹	372.1 \$ t ⁻¹	–	–
EI cost as CO ₂ -eq	87.4 g MJ ⁻¹	173.4 g MJ ⁻¹	–	861 g kg ⁻¹	1843 g kg ⁻¹	2836 g kg ⁻¹	–	–

Table 6 Calculations of EI cost of feedstock and EI credit value of the biorefinery products.

Stream	Fossil-based product	G_f or I_{peq} (as CO ₂ -eq)	Equivalency factor, β	EI from transportation	Calculation
Seeds	–	0.631 kg kg ⁻¹	–	0.001 kg kg ⁻¹	$I_f = 0.631 + 0.001 = 0.632 \text{ kg kg}^{-1}$
Husk	Natural gas	61.17 g MJ ⁻¹	0.8571 MJ MJ ⁻¹	0.001 kg kg ⁻¹	$D_p = 0.06117 \times 19.86 \times 0.8571 - 0.001 = 1.040 \text{ kg kg}^{-1}$
Cake	Soy meal	0.726 kg kg ⁻¹	1 kg kg ⁻¹	0.001 kg kg ⁻¹	$D_p = 0.726 \times 1 - 0.001 = 0.725 \text{ kg kg}^{-1}$
Glycerol	Glycerol	3.708 kg kg ⁻¹	1 kg kg ⁻¹	0.008 kg kg ⁻¹	$D_p = 3.708 \times 1 - 0.008 = 3.700 \text{ kg kg}^{-1}$
Biodiesel	Diesel	2.641 kg kg ⁻¹	1.1150 kg kg ⁻¹	0.008 kg kg ⁻¹	$D_p = 2.641 \times 1.1150 - 0.008 = 2.779 \text{ kg kg}^{-1}$

Table 7 Examples of EVEI analysis calculations.

Stream	Process unit	Calculations
$p4$: husk	1: Dehusking	<p><i>Costs of production</i></p> <p>1. Allocation factor. Streams involved are husk ($p4$) and stream from unit 1 to unit 2 ($f1-2$).</p> $\alpha_{p4} = \frac{P_{p4} \times \text{VOP}_{p4}}{P_{p4} \times \text{VOP}_{p4} + P_{f1-2} \times \text{VOP}_{f1-2}} = \frac{91400 \times 50}{91400 \times 50 + 179800 \times 461.9} = 0.052$ <p>2. Calculation of costs</p> $\bar{C}_{p4} = \frac{[\bar{C}_{f1} F_{f1} + \bar{O}_I] \times \alpha_{p4}}{P_{p4}} = \frac{\left[\frac{[296.3] 271000 + [248166]}{[0.632]} \right]}{91400} = \left[\frac{46.0 \text{ \$ t}^{-1}}{0.098 \text{ kg kg}^{-1}} \right]$
$f1$: seeds	1: Dehusking	<p><i>Values on processing</i></p> $\bar{V}_{f1} = \frac{[\bar{V}_{f1-2} P_{f1-2} + \bar{V}_{p4} P_{p4} - \bar{O}_I]}{F_{f1}}$ $= \frac{\left[\frac{[461.9] 179800 + [50]}{[1.612]} \right] 91400 - [248166]}{271200} = \left[\frac{322.2 \text{ \$ t}^{-1}}{1.42 \text{ kg kg}^{-1}} \right]$

Table 8 Factors for the allocation of costs to products from the feedstock and units in the product paths.

Feedstock or unit	α of outlet stream from process unit in the production path			α of outlet stream at given unit up to the end product		
	Biodiesel	Glycerol	Cake	Husk	Biodiesel	Glycerol
Seeds	1	1	1	1	0.6714	0.0944
Dehusking	0.9478	0.9478	0.9478	0.0522	0.6714	0.0944
Oil extraction	0.8079	0.8079	0.1921		0.7083	0.0996
Transesterification	1	1			0.8767	0.1233
Methanol recovery	1	1			0.8767	0.1233
Decantation	0.8767	0.1233			0.8767	0.1233
Biodiesel distillation	1				1	

Table 9 Example of calculation of economic costs to construct the EVEL costs composite curve of biodiesel

Cost source	Economic cost (M\$ y ⁻¹)	Cumulative (M\$ y ⁻¹)
Feedstock	$(296.3 \times 271200 / (1 \times 10^6)) \times 0.6714$ = 53.96	53.96
Auxiliary raw materials	$(0 \times 0.6714 + 696934 \times 0.7083 + 4926083 \times 0.8767 + 0 \times 0.8767 + 0 \times 0.8767 + 0 \times 1) / (1 \times 10^6)$ = 4.81	58.77
Utilities	$(150477 \times 0.6714 + 2421122 \times 0.7083 + 30015 \times 0.8767 + 1033748 \times 0.8767 + 26113 \times 0.8767 + 261893 \times 1) / (1 \times 10^6)$ = 3.03	61.80
Emissions	$(0 \times 0.6714 + 0 \times 0.7083 + 0 \times 0.8767 + 0 \times 0.8767 + 0 \times 0.8767 + 2057 \times 1) / (1 \times 10^6)$ = 0.002	61.80
Capital costs	$(97689 \times 0.6714 + 745449 \times 0.7083 + 58111 \times 0.8767 + 20949 \times 0.8767 + 23047 \times 0.8767 + 115881 \times 1) / (1 \times 10^6)$ = 0.96	62.76

Table 10 Summary of the effects of modifications on the biorefinery product indicators.

Modification	Biodiesel			Glycerol			Cake			Husk		
	s (%)	$\Delta e \times P$ (M\$ y ⁻¹)	$\Delta i \times P$ (kt y ⁻¹)	s (%)	$\Delta e \times P$ (M\$ y ⁻¹)	$\Delta i \times P$ (kt y ⁻¹)	s (%)	$\Delta e \times P$ (M\$ y ⁻¹)	$\Delta i \times P$ (kt y ⁻¹)	s (%)	$\Delta e \times P$ (M\$ y ⁻¹)	$\Delta i \times P$ (kt y ⁻¹)
Initial	32.2	4.71	94.9	36.2	0.66	14.4	31.5	1.28	17.2	90.4	0.37	86.1
a	44.2	4.71	130.0	48.6	0.66	19.3	48.6	1.28	26.7	93.3	0.37	88.8
a plus b	48.1	5.29	141.5	51.6	0.74	20.5	49.4	1.42	26.9	93.4	0.41	88.9
a to c	50.0	5.32	147.2	53.6	0.75	21.3	52.3	1.42	28.5	93.4	0.37	80.9
a to d	53.4	5.37	157.2	57.2	0.75	22.7	57.2	1.44	31.2	93.3	0.31	70.0

Figure 1 Generic EVEI profile of a product

Figure 2 Biodiesel process simulation model in Aspen Plus[®] and stream mass compositions.

Figure 3 Mass flow rates (F) in kt y^{-1} , VOP, COP and economic margins (Δe) in $\text{\$ t}^{-1}$ along with allocation factors (α) of the streams in a Jatropha-based biorefinery. The economic costs (O_k) of the process units and the cost of methanol and oily waste treatment are in $\text{\$ y}^{-1}$. (O_3' and O_4' indicates calculated values considering the recycled utility stream from unit 4 to unit 3).

Figure 4 Mass flow rates (F) in kt y^{-1} , CVP, ICP and Δi in CO_2 equivalent kg kg^{-1} along with allocation factors (α) of the streams in a Jatropha biorefinery. The EI costs (IO_k) of the process units are in t y^{-1} of CO_2 -eq (IO_3' and IO_4' indicates calculated values considering the recycled utility stream from unit 4 to unit 3).

Figure 5 a) Economic and b) environmental profiles of biorefinery products.

Figure 6 EVEI profile of a) biodiesel, b) glycerol, c) cake and d) husk featuring the costs composite curve ($-\bullet-$), the limiting line (\rightarrow) and the value line ($-\blacksquare\cdot$). Composite curves for each product are constructed as the cumulative EI costs versus economic value from the allocated EI costs of 1) feedstock, 2) auxiliary raw materials, 3) utilities, 4) process emissions and 5) fixed costs, in that order. The process emissions and fixed costs appear together due to relatively small contributions.

Figure 7 EVEI profile of a) biodiesel, b) glycerol, c) cake and d) husk featuring the costs composite curve ($\cdot\bullet\cdot$), the limiting line (\rightarrow) and the value line ($-\blacksquare\cdot$) after the improvements a-c along with the costs composite curve in the base case system ($-\bullet-$).

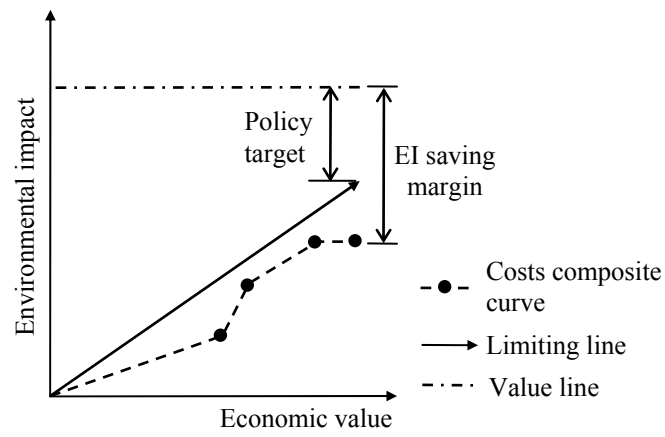
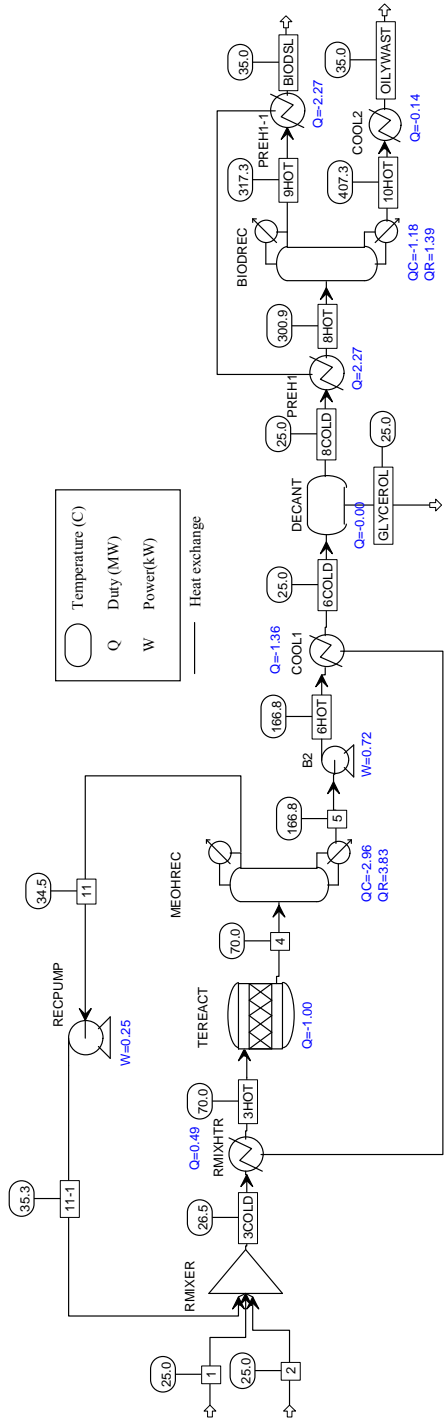


Figure 1 Generic EVEI profile of a product



Stream / Component	1	2	3HOT	4	11	5	8HOT	GLYCEROL	BIODSL	OILYWAST
Triolein	0.4500	0	0.3512	0.0246	0.1171	0.0029	0.0032	0	0.0002	0.0590
Tripalmitin	0.1140	0	0.0833	0.0058	0	0.0072	0.0079	0	0	0.1582
Trilnolein	0.4030	0	0.2946	0.0206	0	0.0255	0.0281	0	0	0.5592
Tristearin	0.0227	0	0.0166	0.0012	0	0.0014	0.0016	0	0	0.0315
Oleic acid	0.0103	0	0.0075	0	0	0	0	0	0	0
Methyl oleate	0	0	0	0.3360	0	0.4149	0.4571	0	0.4769	0.0827
Methyl palmitate	0	0	0	0.0779	0	0.0962	0.1060	0	0.1093	0.0423
Methyl linoleate	0	0	0	0.2752	0	0.3399	0.3744	0	0.3918	0.0447
Methyl stearate	0	0	0	0.0155	0	0.0191	0.0211	0	0.0211	0.0215
Methanol	0	1.00	0.2466	0.1694	0.8823	0.0021	0.0006	0.0169	0.0006	0
Glycerol	0	0	0	0.0731	0	0.0903	0.0001	0.9779	0	0.0010
Water	0	0	0.0001	0.0006	0.0006	0.0006	0.0001	0.0052	0.0001	0
Mass flow (kg h ⁻¹)	13218	1426	18081	18081	3437	14644	13293	1351	12626	667
Molar flow (kmol h ⁻¹)	15.46	44.50	155.18	155.18	95.23	59.95	44.50	15.45	43.43	1.07

Figure 2 Biodiesel process simulation model in Aspen Plus® and stream mass compositions.

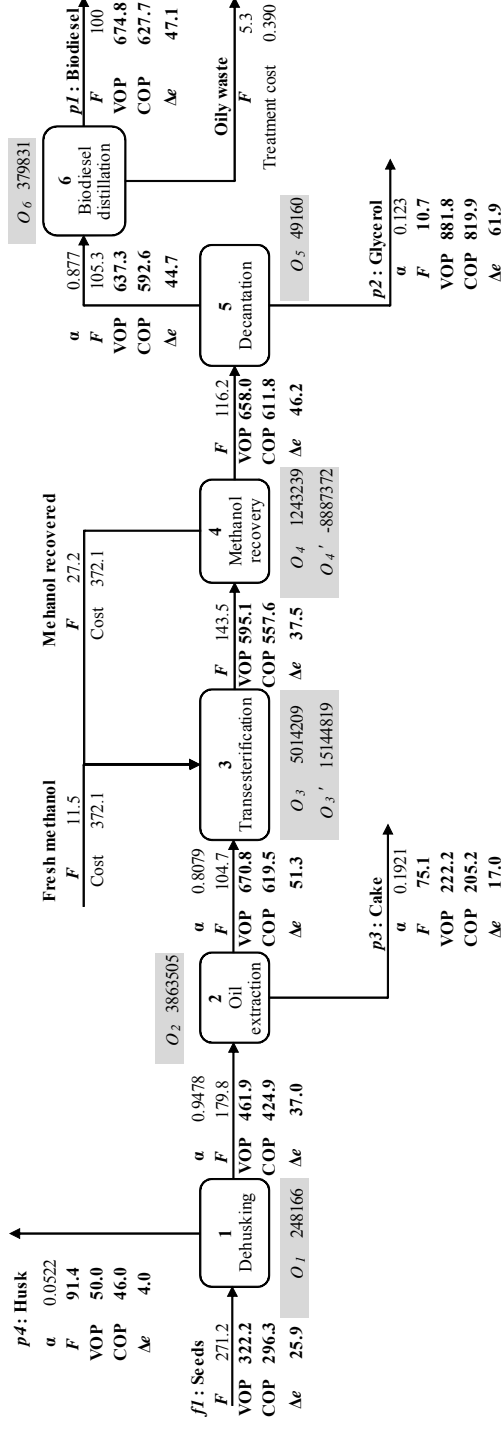


Figure 3 Mass flow rates (F) in kt y^{-1} , VOP, COP and economic margins (Δe) in $\text{\$ t}^{-1}$ along with allocation factors (α) of the streams in a Jatropa-based biorefinery. The economic costs (O_k) of the process units and the cost of methanol and oily waste treatment are in $\text{\$ y}^{-1}$. (O_3' and O_4' indicates calculated values considering the recycled utility stream from unit 4 to unit 3).

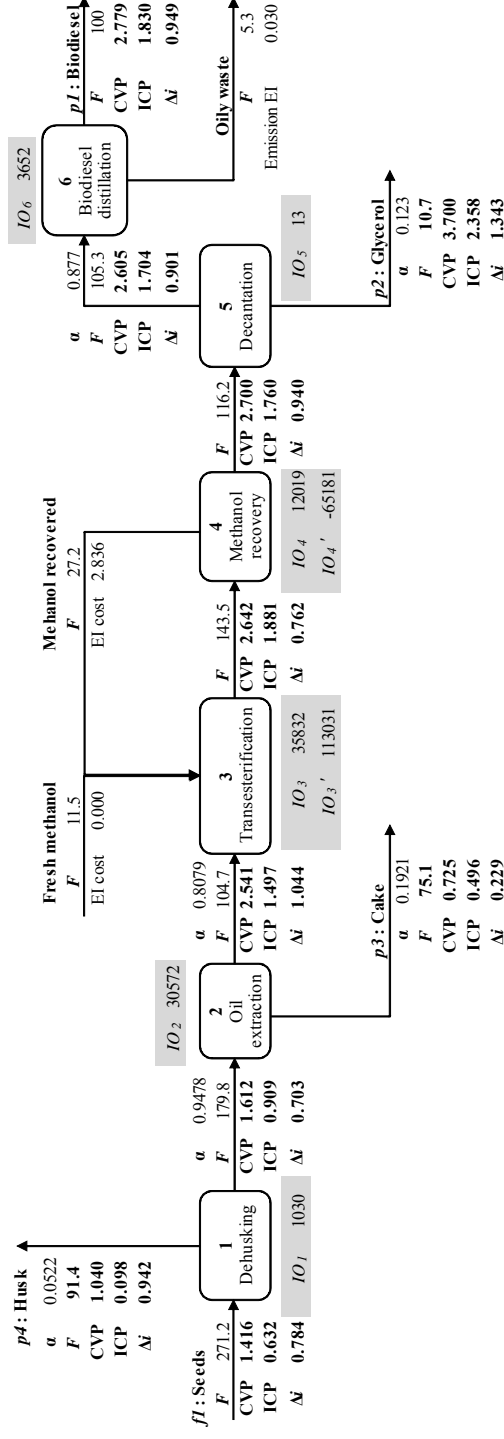


Figure 4 Mass flow rates (F) in kt y^{-1} , CVP, ICP and Δi in CO_2 equivalent kg kg^{-1} along with allocation factors (α) of the streams in a Jatropha biorefinery. The EI costs (IO_k) of the process units are in t y^{-1} of CO_2 -eq (IO_3' and IO_4' indicates calculated values considering the recycled utility stream from unit 4 to unit 3).

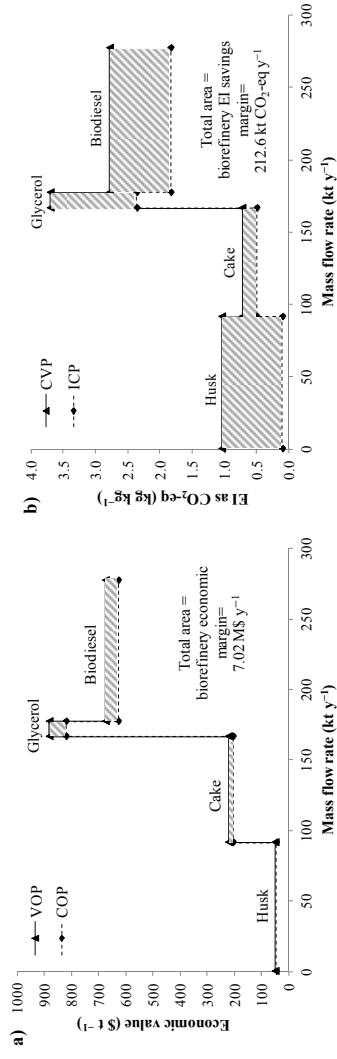
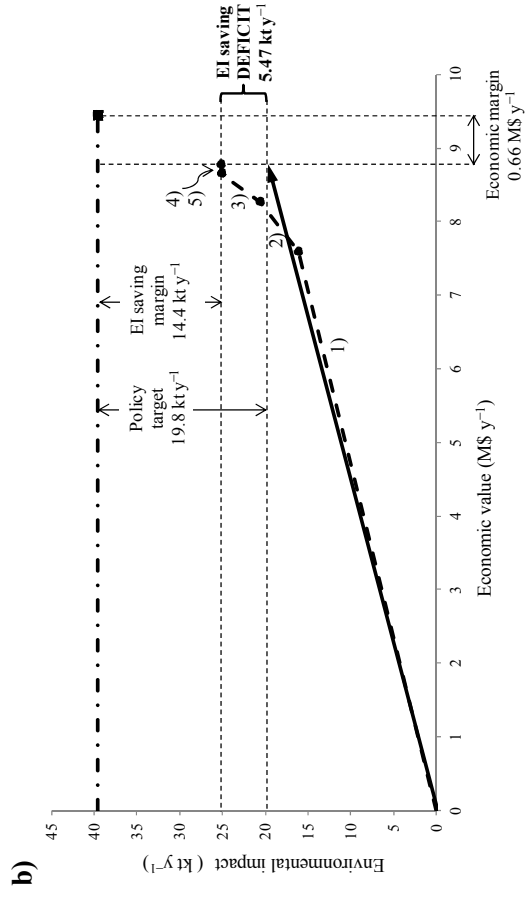
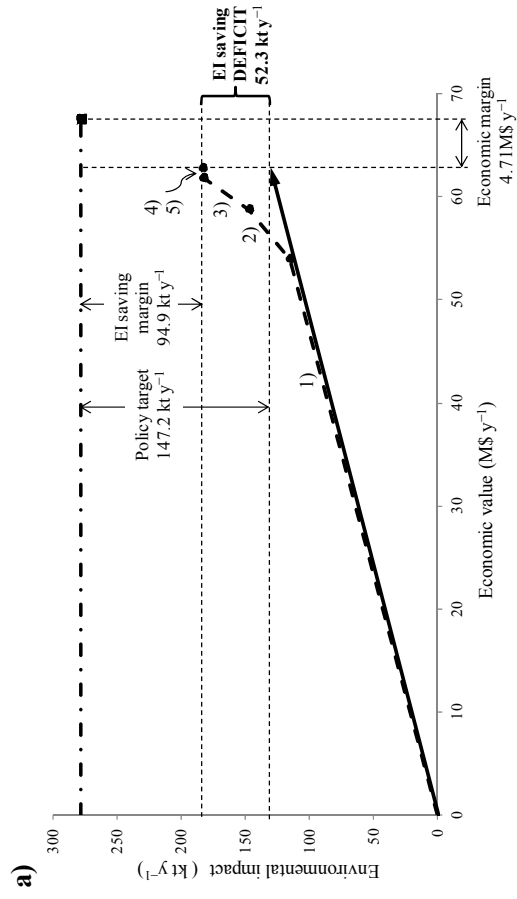


Figure 5 a) Economic and b) environmental profiles of biorefinery products.



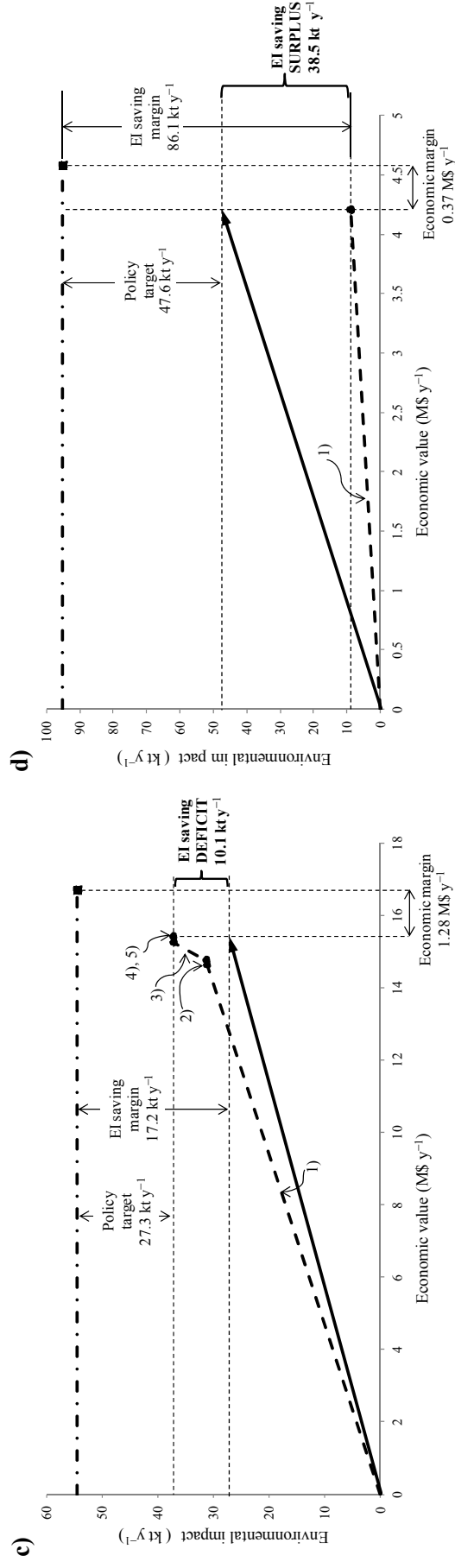
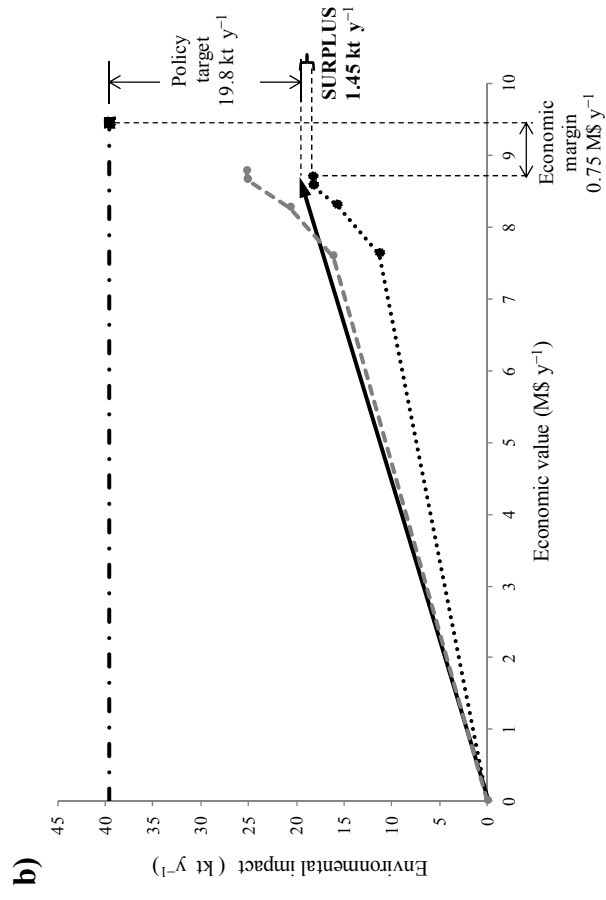
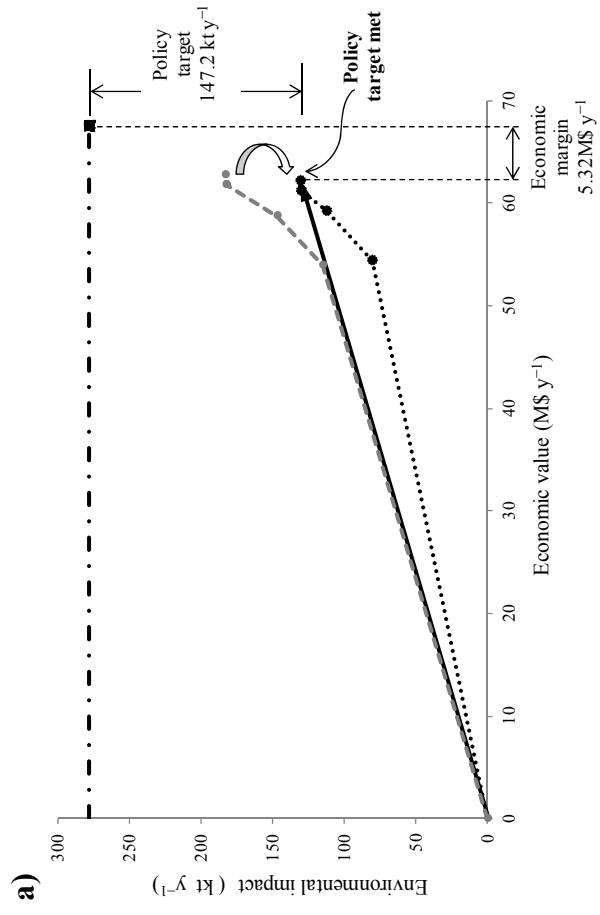


Figure 6 EVEI profile of a) biodiesel, b) glycerol, c) cake and d) husk featuring the costs composite curve (—•—), the limiting line (—→) and the value line (—••••). Composite curves for each product are constructed as the cumulative EI costs versus economic value from the allocated EI costs of 1) feedstock, 2) auxiliary raw materials, 3) utilities, 4) process emissions and 5) fixed costs, in that order. The process emissions and fixed costs appear together due to relatively small contributions.



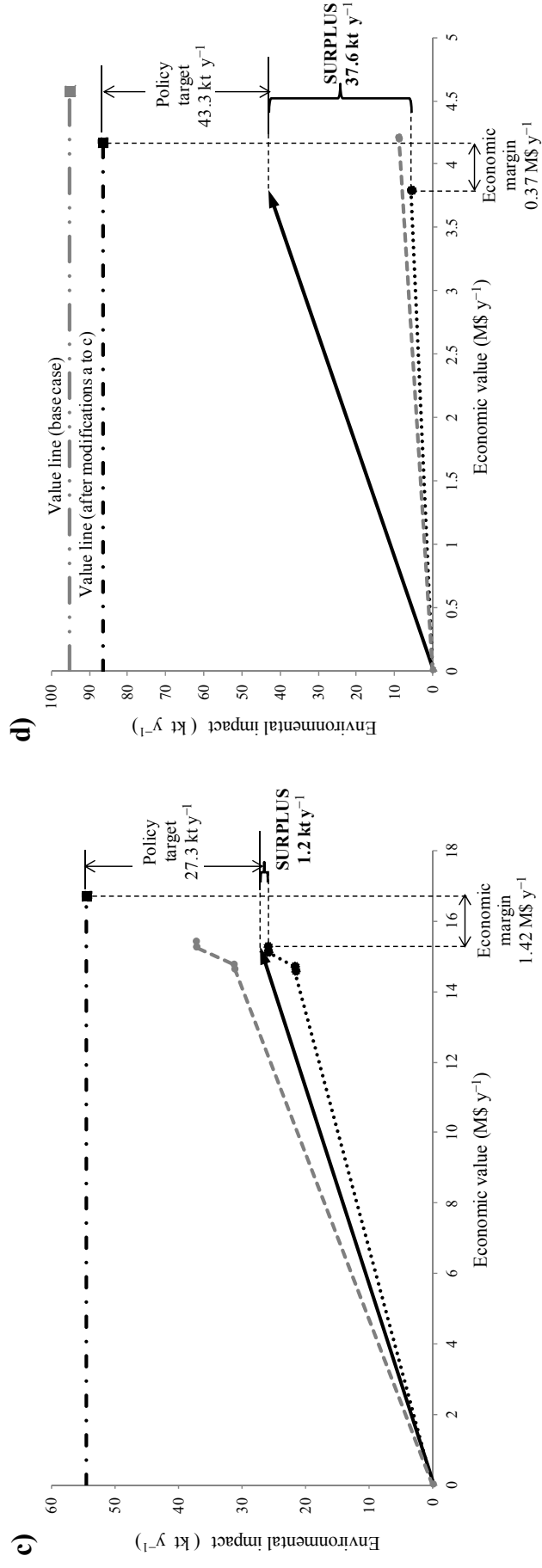


Figure 7 EVEI profile of a) biodiesel, b) glycerol, c) cake and d) husk featuring the costs composite curve ($\bullet\cdots\bullet$), the limiting line (\longrightarrow) and the value line ($-\blacksquare-\bullet$) after the improvements a-c along with the costs composite curve in the base case system ($-\bullet-\bullet$).

Chapter 7

Synthesis, conclusions and future work

7.1 Synthesis of research

In an effort to tackle the critical problems of sustainable development, biorefineries are playing a key role in the shift from fossil resource feedstocks for energy and materials to renewable biomass feedstocks. As discussed in the previous chapters, early biorefinery systems based on biomass conversion to biofuels are sub-optimal, revealing that the standard thinking towards the design of biorefineries must move forward to a framework that would allow biorefineries to *evolve* towards sustainable processing facilities through greater integration and efficiency while also considering compliance with the policy framework.

Extensive contributions have been made to attend the call for the framework previously suggested using process systems tools (Azapagic, 1999; Young et al., 2000; Jensen et al., 2003; Cardona and Sanchez, 2007; Liu et al., 2010; Alvarado-Morales et al., 2009; Kravanja, 2012). Recent works include process simulation and techno-economic studies (Sadhukhan et al., 2008; Hosseini and Shah, 2009; Patel et al., 2011; Ng and Sadhukhan, 2011; Vlysidis et al., 2011; Ng et al., 2013, Heyne and Harvey, 2013), process design and integration (Tan et al., 2009; Ng, 2010; Ojeda et al., 2011; Chen et al., 2011; Fujimoto et al., 2011, Modarresi et al, 2012, Kravanja et al., 2012; Pham and El-Halwagi, 2012), carbon footprinting or GHG balance (Cherubini et al., 2009; Tan and Foo, 2007; Zamboni et al., 2011); sustainability assessment using LCA (Azapagic et al., 2006; Tugnoli et al., 2008; Cherubini and Ulgiati, 2010; Sacramento-Rivero, 2011; Schaidle et al., 2011) and policy implications (Peck et al., 2009; Giarola et al., 2012; White et al., 2013). Other works have tried to combine economic and environmental assessments (Villegas and Gnansounou, 2008; Lim et al., 2008; Ohtman et al., 2010) and to establish

optimisation frameworks for supply chains (Dunnett et al., 2008; Guillén-Gonsálbez et al., 2008; Hosseini and Shah 2011a; Akgul et al., 2012), process design (Sammons et al., 2008; Douglass et al., 2011; Hosseini and Shah, 2011b; Furlan et al., 2012; Ponce Ortega et al. 2012; Martín and Grossman, 2012), etc. However, although these technical capabilities are available, they are often developed separately on a case-by-case basis (i.e. for a particular product, feedstock or processing technology). The available tools need to be used in synergy and readily adaptable to any biorefinery system by following a common integrated framework. In addition, although biorefineries can benefit from process integration tools transferred from their analogous crude oil refineries, such as heat integration, novel developments are also required to address the distinctive issues that are prominent in biomass refining. This recognition of the need for tools to be developed specifically for biorefineries has driven the focus of the research embodied in this thesis.

Building on the previous arguments, the present work aimed to develop tools that allow capturing influential variables at different system levels in order to obtain insights into the performance of biorefinery systems. The insights obtained are then used to improve or produce integrated process designs for better sustainability. As a result, several contributions have been made in this thesis, synthesised as follows.

First, at the very local process integration level, a tool for bioethanol integration based on mass pinch analysis has been developed in Chapter 2. This work showed for the first time how the coupling between processing networks for multiple value-added production generate complex interactions that provide the plot for the generation of innovative approaches for process integration. On this basis, the bioethanol pinch analysis was developed to address this particular scenario within advanced biorefinery schemes. The application of the method along with economic analyses proved to be effective for integration of bioethanol streams in a biorefinery that produces bioethanol and DDGS and uses bioethanol for the production of arabinoxylan (AX) as value-added product.

In a second contribution, Chapters 3 and 4 showed a more comprehensive methodology for biorefinery analysis from the sustainability point of view, integrating the biomass feedstock production system and total site utility system design. At this stage, the work effectively integrated environmental impact

evaluation, specifically in terms of global warming potential from GHG emissions, to assess process integration alternatives. At the same time, process integration strategies were employed to improve the environmental performance of the biorefinery designs.

The work presented in Chapter 5 then proposed a more integrated approach by adding economic analysis to the levels of analysis developed in the previous Chapters, i.e. biomass feedstock production, process design and integration, and environmental impact assessment. As a result, the Economic Value and Environmental Impact (EVEI) analysis methodology was developed from the adaptation and combination of capabilities of value analysis method and life cycle approaches. The new methodology provides a platform of “integrated assessment for integrated biorefineries”.

At an even higher level, the EVEI methodology allowed also the integration of existing policy frameworks, as presented in Chapter 6, particularly for biofuels but in principle extendable to all biorefinery products. A process integration approach was proposed to balance deficits and surpluses of EI savings between products in order to meet policy targets. With the insights provided by this approach, the biorefinery in the case study was retrofitted into a more integrated and energy efficient system with enhanced economic and environmental performances. Thus, high levels of integration seem to be a natural outcome if a plausible policy regime can be established to encourage sustainable biomass processing, diversity in bio-based products and stability in markets.

The contributions from this thesis form a systematic basis for the analysis and generation of highly integrated and efficient processes for enhanced sustainability, informed by biorefinery design and process integration opportunities at the lowest level and by environmental policies at the highest level. An overview of this systems approach can be depicted as in Figure 7.1 in a way similar to the well-known onion model for general chemical process design (Smith, 2005). However, rather than a hierarchical model, the vision of this framework must be of a series of layers integrated between them and as a whole so that “the whole is greater than the sum of its parts”. Notice that the interactions between different levels or layers can be bi-directional.

The thesis first presented work on process network and inter-process integration combined with economic analysis in Chapter 2. Then, the thesis presented work integrating the feedstock production level, process network simulation, inter- and intra-process integration and environmental assessment. In doing so, models were used and developed for LCA of wheat (Chapter 3) and Jatropha (Chapter 4). A yield model was also developed in the case of Jatropha seeds production (Chapter 4). Strategies for intra-process integration for biodiesel, green diesel and gasification processes were also presented. At the inter-process integration level, strategies for synergies between these processes for utility and auxiliary raw material supply were developed. Finally, the research moved in Chapter 5 towards a framework integrating the previous layers within a combined economic and environmental impact assessment methodology. This also provided the opportunity to include the outer layer of policy in Chapter 6.

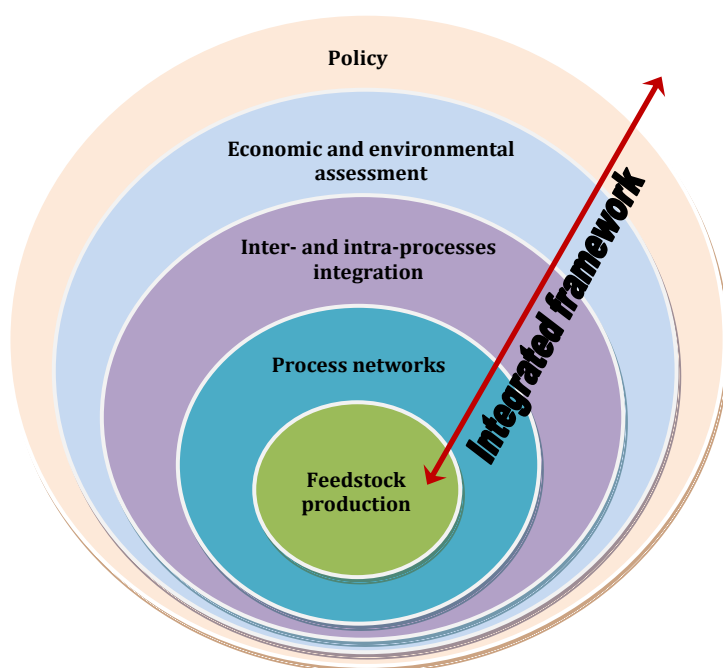


Figure 7.1 An onion model of an integrated systematic framework for biorefinery analysis, design and integration followed in this thesis.

The present work also suggests that whether sugar, starch, oil or lignocellulose are favoured as feedstock or whether a thermochemical or biochemical route proves more attractive, the design of a sustainable biorefinery process must be the result of applying process integration together with economic and environmental impact assessments within an integrated framework as proposed in **Figure 7.1**.

In a vision beyond the grounds of this research, the framework proposed here could be taken forward to constitute a process systems engineering branch known as biorefinery engineering. Biorefinery engineering is a term currently used to name a research group within the School of Chemical Engineering and Analytical Science at The University of Manchester. For instance, if the keyword “Biorefinery Engineering” is typed in Google, the only website result with these two words together is the one from the aforementioned research group. Surprisingly, no formal definition has been provided. Thus, a formal definition of Biorefinery Engineering or, even better, Biorefinery Systems Engineering may be suggested as:

“A discipline providing a methodological framework to address the challenges posed by the planning and design of sustainable biorefineries, from a systematically integrated perspective that accounts for inter- and intra-process integration opportunities together with external interactions and their complexities, ranging from agronomic, physical, chemical, biological, process systems, economic, environmental and policy issues, with emphasis on integration across the life cycle and within and across the system levels or scales”.

Thus, the generic framework of biorefinery systems engineering would allow an integrated vision for the study of biomass production and supply chains, process technology development, energy and utility generation, economic and environmental feasibility studies, etc. Typical tools and methods from the parent discipline, process systems engineering, such as process simulation, heat and mass integration, property integration, etc., can be employed in synergy with life cycle assessment and in new methodological developments for biorefineries as those presented in this thesis. This could be further exploited for superstructure-based modelling, mixed-integer programming, multi-objective optimisation and optimisation under uncertainty.

Similar disciplines have emerged to tackle closely related problems such as energy systems engineering, biological and biochemical systems engineering, industrial biosystems engineering and bioprocess engineering. However, biorefinery systems engineering will not only focus on energy generation and efficiency or biochemical processing of biomass, but on any possible configuration combining any possible processing route, feedstock, platform and products.

7.2 Conclusions

Although biomass was important to supply human necessities before crude oil, over the last century economics favoured the establishment of the latter as the major source of energy, chemicals, materials and other products through crude oil refineries. In the coming years, the combination of resource depletion along with environmental, societal and economic issues discussed in Chapter 1 will re-establish the importance of biomass to satisfy human necessities, but through the new paradigm of biorefineries. Biorefineries have the potential to do so with unprecedented efficiency through extensive and elegant integration. Chemical engineers must be ready with tools that allow a clear understanding of the new challenges associated with biorefinery engineering.

This thesis has aimed to make relevant contributions to the field of biorefinery engineering by adopting and developing tools for process integration and environmental sustainability assessment that, combined, could facilitate the effective and confident generation of sustainable process designs. The scope of this research has been synthesised in the previous section, and the implications within the wider field of process systems engineering has led to the proposal of a formal definition of biorefinery systems engineering. In this section general conclusions regarding each contribution are extracted and synthesised.

Building upon the well established research area of process integration, the thesis first exploits mass pinch analysis for the integration of material streams that could be products as well as in-process working streams. The particular example of bioethanol, which is a major product but also potentially a working fluid, was the stimulus for this line of development. This exemplifies how biorefineries become more complex by introducing co-production pathways in a scenario that has not previously been addressed in this way within this body of knowledge.

As a result of the adaptation of process integration methods to the case of biorefineries producing and utilising bioethanol within their processes, the “bioethanol pinch analysis” was presented in Publication 1 (Chapter 2). The paper demonstrates how the existence of various production lines (bioethanol, DDGS and arabinoxylan in the case study developed) interacting through the exchange (use,

reuse, recovery, recycling) of one of the final or intermediate products within a biorefinery generates the scope for the application of process integration tools to generate designs that use raw material more efficiently while increasing process profitability. The bioethanol pinch analysis approach could be adapted to other situations in which a biorefinery product is also used internally as a process fluid, as suggested in the next section.

Undoubtedly, biorefinery design will benefit from the adoption of energy integration, as exploited by crude oil refineries, to achieve high levels of energetic efficiency and decreased greenhouse gas emissions. But, to what extent can energy integration help reducing fossil-primary energy use and GHG emissions of biorefineries? How could biorefineries achieve self-sufficiency in energy supply? In an attempt to address these questions, a wheat-based biorefinery in the UK was taken as case study as presented in Publication 2 (Chapter 3). Various synergetic schemes for biorefinery processing whole wheat (grain and straw) into bioethanol, DDGS and power were studied using life cycle analysis (LCA) to evaluate the integration options in terms of primary energy use and GHG emissions.

Some key strategies for designing efficient and self-sufficient biorefineries were identified from wheat-based biorefinery case study, which address the questions aforementioned. First, biorefineries must exploit the whole crop in their processes using the lignocellulosic residue (the fraction that is not put back into the soil for nutrient recovery), which otherwise is wasted, to satisfy utility demand. Second, the use of integrated biomass gasification combined cycles (IBGCC) for this purpose offers flexibility in the generation of both heat and power, converting any excess heat into power which can be exported to the electricity grid to generate further environmental and energy credits from replacement. Third, biorefinery product strategies must include the co-production of feed/food to alleviate the food vs. fuel issue. As shown in the case study, the use of DDGS for animal feed replacing soy meal offers better environmental impact credits than its use as fuel or as feedstock to an IBGCC system.

As discussed in Chapter 1, biorefineries must aspire to be highly integrated facilities with self sufficiency not only in energy utilities, but also to be self sufficient in raw materials. The substitution of raw materials with high embodied energy and

GHG emissions intensities by those produced in biorefineries with lower embodied intensities would bring increased sustainability benefits. Using this argument, the Publication 3 presented in Chapter 4 entailed detailed process integration with the aim to reduce overall fossil primary energy use and GHG emissions by producing energy and major auxiliary raw materials on-site. This was achieved following the strategies applied for a whole wheat-based biorefinery.

Using *Jatropha* as main biorefinery feedstock, two integrated systems were explored for the production of diesel-like biofuels (biodiesel and green diesel). The integration strategy included the utilisation of the whole *Jatropha* fruit and especially the utilisation of seed husk (a lignocellulosic residue) for the production of heat and power and the methanol used in biodiesel production or the hydrogen used in green diesel production through IBGCC systems. The further integration of anaerobic digestion of other *Jatropha* residues and process by-products to produce excess bioenergy in the form of power increased the life cycle energy efficiency and reduced the global warming potential. Furthermore, the integration of the process technologies and biorefinery platforms provided enhanced process designs with even negative GHG emissions and primary energy use. This was due to the substantial avoided emissions from replacement of fossil-based energy and raw materials, both internally due to process integration and externally due to the export of excess bioenergy. It was also shown that comparison between the two biofuel systems on the basis of the energy and GHG emissions criteria is not sufficient for recommending the best system for future deployment. Other technological aspects such as infrastructure adaptability of the biofuels might also be relevant to process and product selection. In addition, biorefineries must be able to show economic feasibility to compete with conventional systems. Thus, environmental performance must be considered in conjunction with process and economic performances.

Expanding on the works presented in Chapters 2 to 4, and attending the necessity for integrated analysis of biorefinery systems at multiple levels, this thesis further endeavoured the development of a tool for easy and simultaneous implementation of techno-economical and environmental assessment: the EVEI analysis methodology presented in Publication 4 (Chapter 5). By including process and feedstock production models alongside models at the economic and environmental impact levels, the effects of process integration and co-evolutionary

agronomic and process technologies, economic market and sustainability criteria have been incorporated in to a single methodology. As a result, the simple yet robust methodology is a helpful tool for analysing overall biorefinery performance in a systematic manner. At the same time, it enables insights to be transferred into foresight applications such as scenario building, generation of innovative process integration routes, trade-off evaluation between economics and environmental impact as well as future policy compliance and recommendations.

With respect to policy, as an outer sphere of the context into which biorefineries are to be inserted, the EVEI analysis methodology has been further developed in Publication 5 (Chapter 6). Integrating policy into the integrated analysis framework offers the possibility to guide biorefinery development in a two-way direction: (i) it will help to ensure biorefinery process design and operation is committed to engage with the rules set by policy for sustainability; while (ii) the technological limitations or advantages, found while considering policy constraints, could be informed to policy makers to produce sound and affordable rules that provide favourable conditions for a successful emergence of a bio-economy through biorefineries.

This thesis has laid important foundations for a platform of tools comprising process integration in combination with holistic or life cycle approaches. It is envisaged that this platform will propel generation of ideas for integrated designs and offer solutions to the complex problems produced by the multiplicity of feedstock, processing routes and products, while being conscious of the implications of biorefinery designs for a more sustainable development of our society.

7.3 Future work

The emergence of biorefinery engineering, as a sub-discipline addressing biorefinery and biomass complexities to overcome limitations of existing tools, opens the opportunity for the creation of a plethora of innovations in concept-level synthesis, design and integration, and optimisation of biorefineries. Within this embodiment of knowledge this thesis had made small but distinctive contributions towards a total systems approach for designing the sustainable biorefineries of tomorrow's bio-based

economy. In the same way as the work presented here is founded on previous advances, recommendations for future work are identifiable.

From the work presented in Chapter 2, it is envisaged that the bioethanol pinch analysis approach could be adapted for other similar biorefinery schemes wherein opportunities exist for both inter- and intra-process interactions, through an intermediate or end product. This could be the case of hydrogen which, after overcoming economic constraints, could play a role in future biorefineries as important as its role in current oil refineries. This is due to the fact that some biomass molecules require a degree of deoxygenation to be useful in the current infrastructure. This can be achieved through hydrogenation. On one hand, hydrogen will be consumed to produce paraffins, olefins and aromatics from intermediate platform products such as sugars, vegetable oil, bio-oil and lignin. On the other hand, hydrogen could be produced from gasification of lignocellulose, lignin or products such as glycerol and also from biochemical processing of biomass such as anaerobic digestion. Thus, if a biorefinery built upon the hydrogen exchange network previously described is possible, an opportunity for a process integration tool arises in the same way as it did in the bioethanol network design problem studied in Chapter 2. Other substances with potential for exchange through various processes may include syngas, CO₂, CH₄, etc.

Multi-scale modelling is an approach already applied to biorefineries (Hosseini and Shah, 2011a, b) and other systems. Although the framework presented in this thesis includes the macro-scales from process to policy spheres, it will benefit from the integration of models at the meso- and micro-scale such as kinetic and molecular modelling, metabolic reactions modelling, diffusion models, etc. At this point it is noteworthy that due to its relative simplicity, the proposed EVEI methodology can afford the inclusion of models at all levels of detail and complexity. This is actually highly encouraged to overcome the common drawback in LCA studies of the linearity of transfer functions between inputs and outputs.

Sustainability and the methods for its measurement are still evolving and the data available to evaluate each of the aspects of this multifaceted concept makes it difficult to find information that is easily accessible and transparent. This has largely limited the scope of sustainability studies to energy and GHG emission analyses. The

increasing GHG emissions combined with scarcity and increasing prices of fossil energy resources are arguably the major challenges in our current society, thus the limitation to these criteria for environmental sustainability is justified. However, it is expected that in the future data for more comprehensive studies will become more widespread and accurate, and that the methodologies for evaluation of multiple criteria will become increasingly well defined. This opens another opportunity for future work consisting of the inclusion of various sustainability aspects in a single indicator for EVEI analysis for a better assessment of biorefinery designs. In this respect, water scarcity is an increasingly common problem around the world. Thus, the consideration of water foot-printing in the integrated analysis framework is highly recommended. It is also recognised that results from case studies present uncertainty coming from the utilisation of linear models and data collected from various sources. Accounting for this uncertainty was not part of the scope presented in this work.

Developed after value analysis and life cycle analysis methods, the EVEI methodology inherits the limitations inherent in those methodologies. Therefore, future work is recommended in the direction of reducing uncertainty from data inputs, developing sensitivity analyses and inclusion of methods to automate network decomposition. In another direction, recognising the merits of the aforementioned tools, analytical optimisation strategies could be also developed, similar to those originally presented with the value analysis method or those already presented in literature for life cycle analysis. With such developments, the tools presented here will facilitate both the implementation of integrated biorefinery designs and the cultivation of a generation and community of biorefinery engineers for whom such integrated thinking, across processes and across scales, is their distinctive and defining attribute.

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Appendix

Table A. Detailed mass balance of the bioethanol stand-alone plant analysed in publication 1 and publication 4 (as obtained using spreadsheet model by Sadhukhan et al., 2008)

Equipment	Wheat (t/year)				Process Water	Dextrin	Glucose	Ethanol	α – amylase	Glucoamylase	Hydrogen Peroxide	Sodium Hydroxide	Alcalase	Sulphuric Acid	Yeast	Calcium Chloride	CO2	Total (t/year)
	Starch	Protein	Miscellaneous	Arabinoxylan														
Wheat - Input	864000	142800	169200	24000	0	0	0	0	0	0	0	0	0	0	0	0	0	1200000
Milling (Hammer) - Product	864000	142800	169200	24000	0	0	0	0	0	0	0	0	0	0	0	0	0	1200000
Liquefaction	17280	142800	169200	24000	2208000	846720	0	0	984.00	0	0	6000	0	0	0	1440	0	3416424
Saccharification	17280	142800	169200	24000	2117655	25401.6	911663	0	984.00	1320	0	6000	0	2580.69	0	1440	0	3420325
Fermenter - Liquid product	17280	142800	169200	24000	2117655	25401.6	91166.34	419365	984.00	1320	0	6000	0	2580.69	231.2	1440	0	3019424
Fermentor - CO2 Product	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	401131.91	401132
CO2 Recovery - Product	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	361018.72	361019
CO2 Recovery - Waste	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	40113.191	40113
Centrifugation 1 - Product(ethanol)	3456	28560	33840	4800	1741187	5080.32	18233.3	410978	196.80	264.00	0	4800	0	2064.55	184.96	1152.00	0	2254797
Centrifugation 1 - Product(DDGS)	13824	114240	135360	19200	376467.8	20321.3	72933.1	8387.3	787.20	1056.00	0	1200	0	516.14	46.24	288.00	0	764627
Ethanol recovery - Product	0	0	0	0	1617.503	0	0	402758	0	0	0	0	0	0	0	0	0	404376
Ethanol recovery - Waste	3456	28560	33840	4800	1739570	5080.32	18233.3	8219.56	196.80	264.00	0	4800	0	2064.55	184.96	1152.00	0	1850421
Rotary Dryer 1 - Product	13132.8	108528	128592	18240	26554.23	0	0	0	0	0	0	0	0	0	0	0	0	295047
Rotary Dryer 1 - Waste	691.2	5712	6768	960	349913.6	20321.3	72933.1	8387.3	787.20	1056.00	0	1200	0	516.14	46.24	288.00	0	469580

Table B. Utility requirements and costs of the bioethanol stand-alone plant analysed in publication 1 and publication 4 (as obtained using spreadsheet model by Sadhukhan et al., 2008)

No	Equipment														
		Process Water (t)	Cost of Process Water (£)	Electricity (MJ)	Cost of Electricity (£)	Steam (t)	Cost of Steam (£)	Natural Gas (t)	Cost of Natural Gas (£)	Cooling Water (t)	Cost of Cooling Water (£)	Refrigeration (MJ)	Cost of Refrigeration (£)	Total annual cost of utilities (£)	
1	Milling (Hammer)	0	0	34214400	410572.80	0	0	0	0	0	0	0	0	410,573	
4	Liquefaction	2208000	1324800	7682543.7	92190.52	254837.94	1783865.5	0	0	0	0	0	0	3,200,856	
5	Saccharification	0	0	2572357.3	30868.29	0	0	0	0	2923682.642	43855.24	0	0	74,724	
6	Fermenter	0	0	13733626	164803.51	0	0	0	0	10000519	150007.78	0	0	314,811	
7	Centrifugation 1	0	0	28641213	343694.56	0	0	0	0	0	0.00	0	0	343,695	
8	Ethanol recovery	0	0	4402356.5	52828.27803	603813.41	4226693.8	0	0	17647058.82	264705.8824	0	0	4,544,228	
21	Rotary Dryer 1	0	0	28641213	343694.56	0	0	20994.81	2624351.70	0	0	0	0	2,968,046	

Table C. Mass and energy balance of straw CHP plant and environmental impact results as obtained from the spreadsheet model (developed in this work after Ibrahim (2010) and Sadhukhan et al. (2009))

Concept	Flow rate ton/year	CPE MJ/year	GWP ₁₀₀ kg CO ₂ eq./year	EP kg PO ₄ ³⁻ eq./year	AP kg SO ₂ eq./year	ARU kg Sb eq./year
RAW MATERIALS						
Wheat straw	360905	0	0	0	0	0
Boiler feed water	60963					
PLANT EMISSIONS						
Ash	31599		27966	1618933	-	-
Waste Water	35540			0.46	3	-
Flue Gas	1848104		484574746	131	708	-
TOTAL from emissions			484602712	1619065	710.27	
PLANT CONSTRUCTION						
Steel	554	24251992	1195082	336	7952	21
Concrete&cement	505	3133107	14529	0	3	-
Activities and decommissioning			302679	84	1989	-
Transportation	120 km		4858	2	14	99
TOTAL construction		27385100	1517148	423	9957	120
TRANSPORTATION						
Straw transportation	25 km	6263377	383959	149	1251	16866
TOTAL CHP PLANT		33648477	486503819	1619637	11919	16986
Total per ton straw		21195	306442	1020	8	11
NET ENERGY PRODUCED	kW	GJ/year				
Electricity (MJ)	54682	1377980				
Heat	29241	736882				