Chemical Biorefinery Perspectives

The valorisation of functionalised chemicals from biomass resources compared to the conventional fossil fuel production route

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Proefschrift

ter verkrijging van de graad van doctor
op gezag van de rector magnificus
van Wageningen Universiteit,
Prof. dr. M.J. Kropff,
in het openbaar te verdedigen
op vrijdag 24 oktober 2008
des namiddags te half twee in de Aula

"Anyone who believes exponential growth can go on forever in a finite world is either a madman or an economist."

- Kenneth E. Boulding (1974)

Dissertation Abstract

In response to the impending problems related to fossil fuels (continued supply, price, and regional and global pollution) alternative feedstocks are gaining interest as possible solutions. Biomass, considered sustainable and renewable, is an option with the potential to replace a wide diversity of fossil based products within the energy sector; heat, power, fuels, materials and chemicals. All the proposed applications for biomass, however, require direct and indirect fossil derived inputs. The maximum fossil fuel replacement potential of various biomass systems and biorefinery concepts were determined using life cycle analysis (LCA) tools. Yet, as opposed to a traditional LCA, the calculation matrix developed here revolves around energy flows and was extended to incorporate process efficiency in terms of exergy, essentially compiling a comparative exergetic cradle-to-factory gate analysis. Inclusion of exergy calculations requires a greater understanding of the processes and reveals that several previous assumptions towards agricultural systems are no longer suitable for non-biomass applications. It also revealed that by upholding the functionality of the biochemicals present in biomass for use as chemical products and precursors, sizeable reductions of fossil fuels can be achieved. Oriented towards existing bulk-chemical products, the analysis was expanded to systematically determine the optimal biorefinery cropping system from 16 common bioenergy crops in their corresponding regions. Although no concrete optimum was determined, the results all led to the conclusion that other biomass systems based on combustion or conversion to combustible products are sub-optimal in comparison. The best application of biomass for the replacement of fossil fuels is the petrochemical industry.

Dissertation Layout

Preface

Introduction to background and rationale for chemical biorefineries

Setting the scene

„Die Zukunft ist kein Schicksalschlag sondern die Folge von Entscheidungen die wir heute treffen"
(The future is not an ordeal of fate, but the result of decisions we make today)

- Franz Alt (1905)

This is merely one of the lesser known quotations related to the future. Infinitely more famous and written for a secondary school essay themed *"my future plans"*, Albert Einstein wrote *"A happy man is too satisfied with the present to dwell too much on the future"*. This best sums up the doctrine and mindset of our current society; why bother about the future? Since the end of the Second World War, societies of the western hemisphere have largely sustained continuous peace, prosperity and have enjoyed unprecedented leaps in technology and product developments, all of which has enabled our society to become vastly affluent consumers seeking out leisure and entertainment. Governments, businesses and citizens alike have become entranced with the notion that the status quo will endure without dwelling too much on the future. Business-as-usual practices with an increasing tendency for short-term investments and risky credit policies are also becoming the norm. The question that arises is sustainability; how long can this growth continue? To understand this one must dare to ask: *How was it possible in the first place?*

Naturally there are a multitude of factors, but there is one common underlying reason: a multigenerational period of a sheer abundance of practically everything, all made possible by cheap energy sources. We are now reaping the benefits of earlier decisions to extract and exploit fossil fuels. To avert calamity and peril we must immediately begin to make intelligent and coherent long-term strategic decisions towards a future based on scarcity. Not only will this involve a paradigm shift of epic proportions but it will also require precise assessment of the new paradigm to achieve maximum impact. The old system and the impending problems must be clarified before discussing solutions:

Current paradigm

The energy sector

> Fossil fuels include coal and lignite, oil shales, and tar and asphalt, as well as petroleum and natural gas, have all had their origin from plants and animals existing upon the earth during the last 500 million years.

While traceable to the emergence of the industrial revolution and clearly visible for more than a century, the blessings of the last decades have been made possible by the sheer abundance of energy. External energy present in such great concentration and availability made it possible to eliminate drudgery while exponentially increasing productive output. This energy is exploited by large from fossil fuels. As an example, the current energy situation in the Netherlands is shown

(Figure 1). It graphically illustrates the total energy sector import and export flows of crude oil, refined oil, gas, coal, nuclear, electricity, heat, and renewables along with their respective local consumption sectors. Even though with Rotterdam and the North Sea, the Netherlands does have a unique infrastructure of crude oil cracking and natural gas processing (i.e. industry), this construct is fairly representative throughout the developed world.

Figure 1   Dutch Energy Sector Schematic (ECN)

A closer look into the domestic consumption rates assists in creating the following distribution charts (figure 2). While most non-experts and civilians commonly associate fossil fuels with transportation fuels at the pump (i.e. petrol and diesel) it represents only 19% of the sector. Even though actual distribution figures are country and region specific, the industrial requirements are still typically high (20 – 50%) and, as indicated above, fed by all the different fossil fuels.

Figure 2   Dutch Energy Sector Distribution (ECN)

Further analysis of the energy use distributions reveals that 15% of the Dutch energy sector is directed towards the chemical industry. Being one of the worlds largest petrochemical clusters, the port of Rotterdam processes large volumes of oil-based and gas-based products, thereby providing a major source of income and employment for the country. Although the significance of the petro*chemical* industry within the energy sector is frequently overlooked, it consumes worldwide around 7.5% of total global energy production (IEA). The petrochemical industry is reliant upon fossil fuels for its source of feedstock and for its internal process energy generation.

Peak oil and possibly more

The concern that may evolve into a serious problem is that according to the Malthusian theory there are physical limits to growth in a finite system. Best described using the *bacterial growth model*, after the log phase (exponential growth) and stationary phase, bacteria enter their death phase as resources become exhausted. Despite these, the current doctrine and mindset of our society is that growth (e.g. economic, population, energy consumption and production, etc.) will continue without decline. Practically all politicians, economists, governmental and non-governmental organisations still believe in an unabated continuation of growth. However, public conception seems to be rapidly changing as scientist are speaking up, warning that continued growth is impossible on a finite planet and signs are already indicating that the stationary phase is close. Figure 3 shows global crude oil production according to IEA-data history of those oil producing nations that have peaked or have most likely peaked. The peak is analogous to the stationary phase and was originally termed *"the date of the culmination"* when investigated for all fossil fuels by M.K. Hubbert in 1956. With regards to oil it is now called *"Hubbert's peak"* or simply *"peak oil"*. The actual date of global peak oil is unknown as the most recent production statistics saw a slight increase during the first quarter of 2008. It is however apparent that continued production growth of crude oil and the other fossil fuels is implausible. Peak oil is very near, signifying the impending resource shortages.
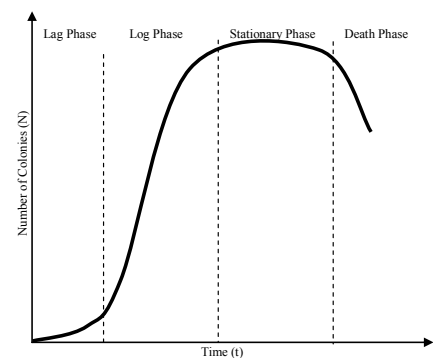
Whilst the exact date of peak oil is still open to debate, the current spiralling trend of the world oil market price is not. On the left-hand of Figure 3 is the crude oil price history until March 2008. In September 2004, the price of Brent crude oil was 40$/bbl and by July 2008 had reached 144$/bbl, while dropping to a still near 3-fold increase of 105$/bbl at the time of print. Studying the two graphs side-by-side strongly supports the suggestion that price is a function of peak realization rather than speculation as is often claimed. Any interruption in the production *growth* output of fossil fuels will have an effect in the broad energy sector. Other fossil fuels, while further away from their respective peaks, are interlinked with one another; as crude oil prices rise, all energy prices rise.

Price shocks are early signals indicating that the stationary phase has occurred and that unless abundant replacement resources are found decline is inevitable. *But,* if there is one thing that is in ample supply and unlikely to peak shortly, it is human ingenuity to adapt and overcome obstacles.
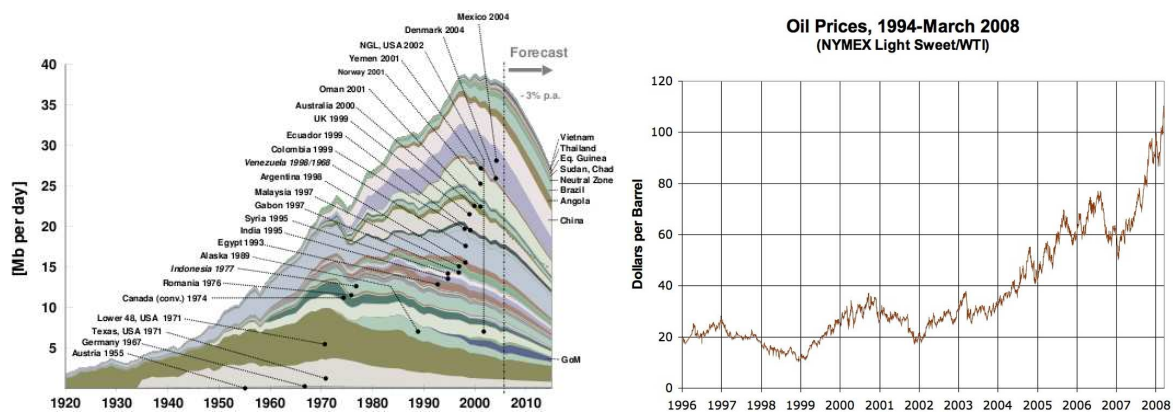
Figure 3   Global Crude Oil Production History & Forecast and Crude Oil Price History

Future paradigm

Sustainable alternatives

Our current obstacle is achieving sustainable development; economic, environmental, and socio-political sustainability. The term is the product of the Brundtland Commission which first conceptualised the meaning. Their definition has since become the most cited explanation of sustainable development in the field of alternative energy resources.

> ## Brundtland Commission (1987) – Sustainable Development
> *"meet the needs of the present without compromising the ability of future generations to meet their own needs"*

To be sustainable, the resources needed to replace fossil fuels must be renewable (i.e. without their own peak) and be of a sufficient abundance to ensure stability. There are countless numbers of alternative energy technologies developed, under development and hypothesized. Those classified as existing are generally familiar; including photovoltaic cells, wind energy, geothermal energy, biofuels, etc. There are also less familiar emerging technologies; such as organic solar cells, tidal energy, algae propagation, advanced biofuels, etc. They are all part of the same collective goal aimed at creating a *"post carbon economy"*; an economy in which the fossil fuel component of the energy sector is replaced. Rather ironically, in the rush to capture grant and subsidy money along with public attention, scientists, industrialists and stake holders alike resort to competitive disagreements, whereas traditionally the intellectual "battle" is fought between the followers of the new paradigm (post carbon economy) and the reluctant hold-outs of the old (fossil fuels). None of the replacement resources are in sufficient abundance to cover the energy sector in its entirety, therefore all technologies must be combined in a collective effort.

Biomass

Many in the field of biomass claim it to be *the* renewable resources to replace the entire energy sector with studies regularly investigating the maximum availability of biomass in relation to regional and global energy consumption rates. The term *"biobased economy"* even insinuates its

capacity of replacing all aspects of the traditional fossil fuel-based economy. It would be presumptuous to assume that biomass will be able to completely cover the worlds energy needs,
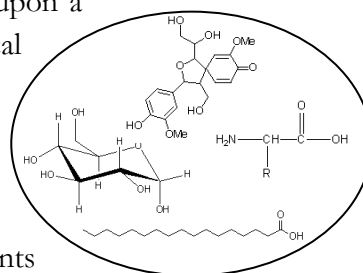
Biomass is any organic material made from plants or animals. Domestic biomass resources include agricultural and forestry residues, municipal solid wastes, industrial wastes, and terrestrial and aquatic crops grown solely for energy purposes. (DoE)

but is can contribute to a large portion of the post carbon economy. Considering that biomass can indeed be applied for a wide variety of purposes it is imperative to strive for options with the maximum efficiency and resource replacement potential. Preindustrial applications of biomass (e.g. wood) were used to generate heat through direct combustion. Early industrial applications of biomass (e.g. barley) were used for conversion into alcohol. Similar principles are currently employed using modern techniques for transportation fuels, nonetheless biofuels are not the most efficient option available. Modern biomass combustion systems have achieved leaps of efficiency improvements while also contributing to electricity generation, nonetheless bioenergy is also not the most efficient option. Applications based on direct or indirect combustion of biomass is a start, but is not the most effective method in contributing to the new paradigm.

Biomass best for the chemical biorefinery

There is one fundamental difference between biomass in contrast to all other alternative energy sources, namely chemical functionality. Biomass is based upon a carbon backbone and contains many other interesting chemical functionalities. All the other renewables are based on heat and electric generation. This raises the question of why to use the chemical energy potential for combustion purposes? Applications should be focused on best employing the unique properties of biomass. And as mentioned above, the chemical industry represents quite a significant portion of the energy sector. Currently, with exception to the pharmaceutical industry and several other niche chemical industries, biomass is hardly used as a chemical feedstock. Nonetheless, biochemicals are the most efficient foreseeable option for biomass to contribute to a reduction of the fossil fuel component in the energy sector. This means narrowing down the biobased economy to a more defined core-business. Figure 4 depicts the current petrochemical industry for a cluster situation (in this case Rotterdam). It indicates that as the chemical functionality (derivatives) increases, the production volumes decrease and the market price increases. In this industry, and especially for the lower derivates, price and energy (fossil fuel) intensity are directly related. One could then argue that products from chemical biorefineries are best suited for sector entry at the higher derivates. However, this approach may conflict with the profitability and feasibility of the industry, as all the upstream processing facilities would eventually be made redundant. In addition, it is of utmost importance to ensure the compatibility of the downstream industries, meaning the existing chemical products are best maintained (i.e. no new biochemicals). As a result the best entry position is near the beginning stages (bulk chemical) of the petrochemical scheme; both utilizing biomass' unique chemical functionality and maintaining the industry's infrastructural downstream investments.
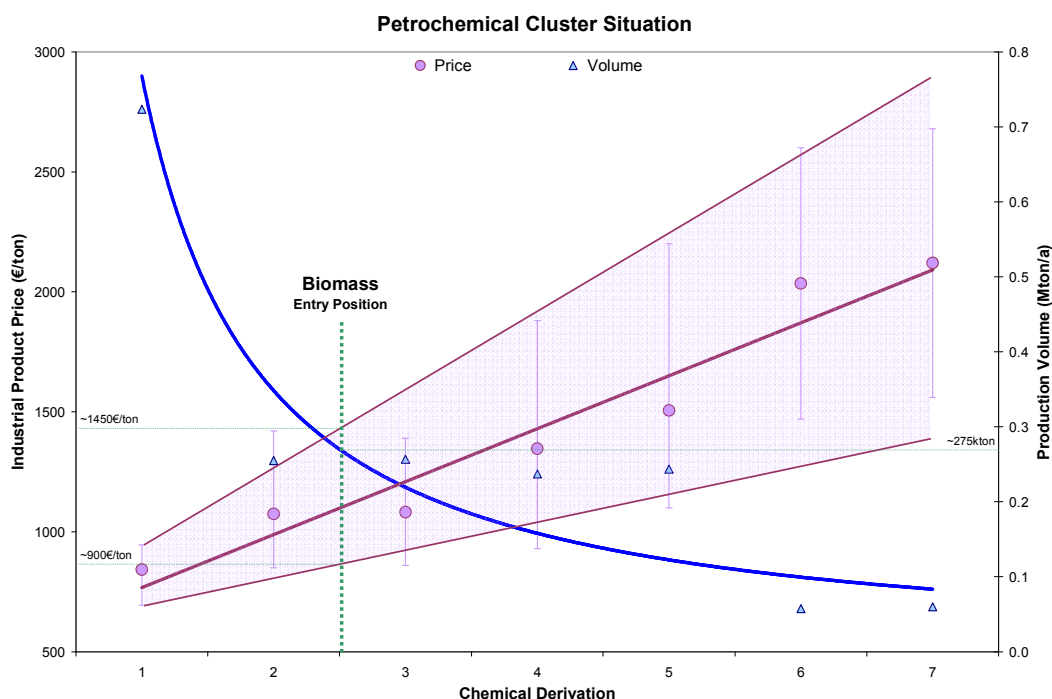
Figure 4   Current Petrochemical Sector Situation in Rotterdam
- Based on data from the Port of Rotterdam and Icis-Pricing as of mid-2008

The paradigm shift

Focus on maximum potential

Each of the alternative resources will have a specific role and niche in maximizing the paradigm shift from the fossil fuel-based energy sector to the sustainable zero carbon economy. The best employment options in replacing great quantities of fossil fuels from biomass is in substituting the petrochemical industry's feedstock. Biomass cultivation, harvesting, transport and processing are all energy intensive steps which can jeopardize the validity of these statements. Its "best" use must be properly assessed. Therefore the maximum fossil fuel replacement potential of various biomass systems and biorefinery concept were determined using life cycle analysis tools.

Strategic foresight

Baruch Spinoza philosophised that experience can made valuable when, by imagination and reason, it is turned into foresight. Fortified by foresight plus a collection of developed tools and know-how, a careful and strategic plan can be composed to best tackle the impending resource shortages to ensure a sustainable development. But before rash decisions affecting the future are made, each replacement option must be properly assessed for its maximum impact in positively promoting the transition. In this dissertation, to obtain my doctorate of philosophy, I have philosophised and calculated how to incorporate biomass in the most intelligent way possible in a future faced with fossil fuel scarcity.

Chapter 1 - Introduction

Methodology description behind implementing an energetic and exergetic cradle-to-gate analysis for valorizing the optimal utilization of biomass

1

Abstract

Biomass has the potential to replace a wide diversity of fossil based products within the energy sector: heat, power, fuels, materials and chemicals. It is considered sustainable and renewable, yet in all the potential applications for biomass, direct and indirect fossil derived inputs are required. Investigating the best possible utilization options for biomass necessitates life cycle thinking to determine the amount of fossil fuel energy replaced in each system. The methodology and significance of using an energetic and exergetic cradle-to-factory gate assessment is described for common biomass crop production routes and biorefinery layouts using Dutch sugar beet as an expletory crop. Preliminary results indicate that the optimal utilization for biomass is for chemical biorefinery concepts.

1.1 Biomass and Sustainability

1.1.1 Fossil Fuels

Plant matter has the capability to convert incoming solar radiation directly into glucose and indirectly into other organic chemicals. Highly abundant, highly dense, and highly energetic hydrocarbons have been formed through the collection and fossilization of plant matter. These fossil fuels: coal, natural gas and crude oil (to name a few) have facilitated the industrial revolution, the advancement of the developed world, and our high quality of life. Fossil fuels being relatively cheap and energy rich have since formed the foundation of our civilization.

> Consider[1-4]: The food intake of a worker doing a 12 hour shift is equivalent to 8.4MJ whereas a barrel of crude oil (at 0.853kg/l and 44.9GJ/ton) is 6.09GJ meaning a barrel of oil is equivalent to around 2 years of food energy intake for an overworked labourer. The Great Pyramid of Giza is believed to have taken 20years and 300000 overworked labourers (slaves) to complete. In terms of oil equivalent this is 1.5Mbbl, which is less than 3 days current consumption of Egypt. Furthermore, modern machines are considerably more efficient (45%) than labourers in converting energy into work (1-10%).

This thinking logic has been extended and brought into some humorous and alarming calculations; coined by Boyden[5], following current fossil fuel consumption the average European requires around 100 energy slaves. Regardless of how it is presented the advanced societies are making good use of available fossil energy to such an extent that practically all fields of human activity are directly or indirectly coupled to their implementation. The addiction to oil is not only limited to the US, as recently stated by President Bush[6], but the entire industrialised world. Exploiting fossil fuels provoke local and global environmental problems, such as pollution and the emission of greenhouse gases[7]. Analogously to smoking, continued use causes health problems, while smokers have the choice to withdraw from the habit usually in an abrupt and complete fashion, withdraw from the fossil fuel habit will probably *not* be of free choice but follow the production decline curve path as indicated by of Hubbert's peak theory.

1.1.2 Sustainability

There is no doubt that fossil fuels power our civilization and that looking for alternatives to compete economically is a major challenge. Economic considerations are rarely the only questions that arise when discussing alternatives; are the environmental problems reduced, are they renewable (directly or indirectly using solar radiation), and do they have the potential to be abundantly available? The Brundtland Report[8] is well-known and credited for coining the term *"sustainable development"*. The definition being: *"sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs"*. This could be interpreted as continuing our reliance on vast amounts of energy, but with as little fossil fuel and other non-renewable sources as possible. There is still considerable time to conduct research into the different sustainable directions aside from more efficient handling of existing resources. Research and development should be directed at those technologies with the least reliance on direct and indirect fossil fuel input, adhering to sustainable development practices. However,

none of the currently proposed renewable energy technologies are completely sustainable, as they are not completely void of fossil fuel input. These non-renewable energy sources are ultimately required at some point along the process chain. A term used to explain the total amount of embedded non-renewable energy in proportion to the renewable energy is the net energy value (NEV). Inverted and expressed as a fractional percentage of the product is the energy breeding factor (BF); lowest fraction being the most sustainable option[9].

1.1.3   Biomass

Biomass is essentially un-fossilized plant matter that can in theory (and already to a degree in practice) substitute all fossil fuels, in particular naphtha products. Major limitations in biomass production are arable land space (or shore-space), water, nutrients and solar radiation. To overcome these and the expensive land cost of fertile land high yields are necessary. High yielding modern agriculture has become energy intensive: in the form of fertilizers, irrigation, ploughing, harvesting, etc. Sea based biomass (e.g. algae), while presenting a unique solution to the land constraint, is not void from indirect fossil fuel input. Land based biomass, understood as plants or crops, are dedicated for non-food purposes such as in the form of renewable energy. In more recent studies, it is suggested to use many other organic sources; wastes from humans (sewage and household disposal), animals (manure), agriculture (straw, leftovers), food processing (rest fats, expired goods), essentially any renewable bioresource[10]. The field of biomass is limited to the existing and emerging applications, but can already be categorized: bioenergy, biofuels and biochemicals. Any of the traditional fossil fuel products and applications derived from biomass will bare the *"bio"* prefix. Proving alternative solutions for all aspects of the energy sector is known as the *"biobased economy"*. Regardless of the category, non-renewable energy is required somewhere along the process chain (e.g. cultivation, harvesting, preparation and conversion). Nonetheless, to displace a form of fossil energy each biomass production route requires some smaller input of another fossil fuel energy. The breeding factor will vary for each potential biomass category and the specific biobased product (biorefinery). Since the breeding factor is a ratio it is inherently limited in practice, but by relating it along with the potential production yields based on cropping data, the fossil fuel mitigation per arable land area (i.e. GJ/ha) can be determined. Biomass, much like crude oil, is not limited to a single product but can be processed to yield wide spectrum of viable products in a so-called *"biorefinery"*[11, 12]. Technically biosyngas facilities can be classified as biorefineries because they produce a wide range of products (biohydrogen to biocrude), even though they are produced from the simple gasifying building block products (hydrogen and carbon monoxide). In this text, biosyngas facilities are not understood as a biorefinery, but as a type of biomass application. Multiple chemical product biorefinery configurations are suspected to mitigate the largest amount of fossil fuel, but can only be validated by employing life cycle thinking. It requires detailed assessment of each part along the process chain independently and combined to depict the whole picture. Already today with existing, modern, and state-of-the-art methods and technology large fossil fuel mitigation is possible with the proper configuration of the process chains in relation to a biorefinery. Each of the biorefinery categories must be subjected to the same degree of assessment detail to yield

consistent and comparative results. The assessment will also determine if upholding the unique chemical functionality of biomass for chemical production has a beneficial effect on the overall fossil fuel replacement potential.

1.2 Methodology

1.2.1 ISO14040 Series

The Society of Environmental Toxicology and Chemistry (SETAC) has defined Life Cycle Assessment (LCA) as *"an objective process to evaluate the environmental burdens associated with a product, process, or activity by identifying energy and material used and wastes released to the environment, and to evaluate and implement opportunities to affect environmental improvements"*. LCA's are vague per definition with countless numbers of different methodologies existing and continuously being developed. Nonetheless, many have been nationally and industrially standardized. In 1997, the International Organisation of Standards (ISO) produced a detailed set of standards that LCA practitioners should adhere to unifying national, industrial, and commercial standards: the ISO14040 series is the current standard. Although considering the vast scope, differences in execution and a large potential for personal influence deem it more a guideline than a true standard. Commonly referred to as a recipe, like a cookbook, the ISO14040 systematically lists procedures and considerations to follow for the intended application as described per the goal and scope[13].

1.2.2 Goal and Scope

There are many types, forms, and impact categories possible following the ISO14040 series. Many of the subsequent procedures and considerations have been designed to focus on ecological and environmental assessments. These will not be conducted herein as they are to a large degree bias, misleading, and heavily reliant on personal interpretation. The main goal of this investigative methodological assessment is to determine the application of biomass with the highest potential mitigation of fossil fuels. The considerations can be narrowed-down and directed towards material steams, cumulative energy, and its thermodynamically efficiency factor…exergy. The significance of exergy will be explained later. All the different types of energy input, for example steam and electricity, are brought back to the original processed fossil fuel. As the analysis will be used as a tool to determine the replacement of fossil fuels, exploration, processing, and refining costs of fossil fuels can be negated as those processes are present in all scenarios and layouts. For the major material streams the extraction and processing must be considered and related to initial fossil fuel input; affectively setting the *"cradle"* at the virgin state. Cradle-to-grave analysis is a synonym commonly applied to LCA's. It entails comparisons of at least two different products that follow separate disposal routes, hence extending the assessment to the *"grave"* or to the end of the life cycle. As bioenergy, biofuels, and biochemicals are employed as potential replacements for existing industries and infrastructures there is a common point of cohesion. Dubbed the *"factory gate"*, all processes, emissions and eventual disposal are identical from that point onwards. Some additional considerations are nevertheless required, i.e. the different chemical energy content of bioenergy and biofuels when released upon combustion.

A chemical biorefinery will not necessitate such considerations as long as the final chemical products exist. An *"exergetic cradle-to-factory gate comparative assessment"* is performed with the goal of determining the best application for biomass to replace the maximum quantity of fossil fuels. All values will be expressed in GJ, ton, ha, and for simplification purposes barrel of oil (bbl). The functional unit for comparison is a ton of final product (biomass side).

1.2.3   Inventory

Figure 1 outlines the processes involved in producing the chemicals (or other products) from biomass. The dotted line is used to highlight those inputs and processes which require prime energy and material use, i.e. fossil fuels. Each input is investigated to such detail that the original fossil fuel input can be determined in relation to the crop output figures. Crop yields are regionally dependent and directly influence the prime and secondary input categories due to required agronomic input relation.
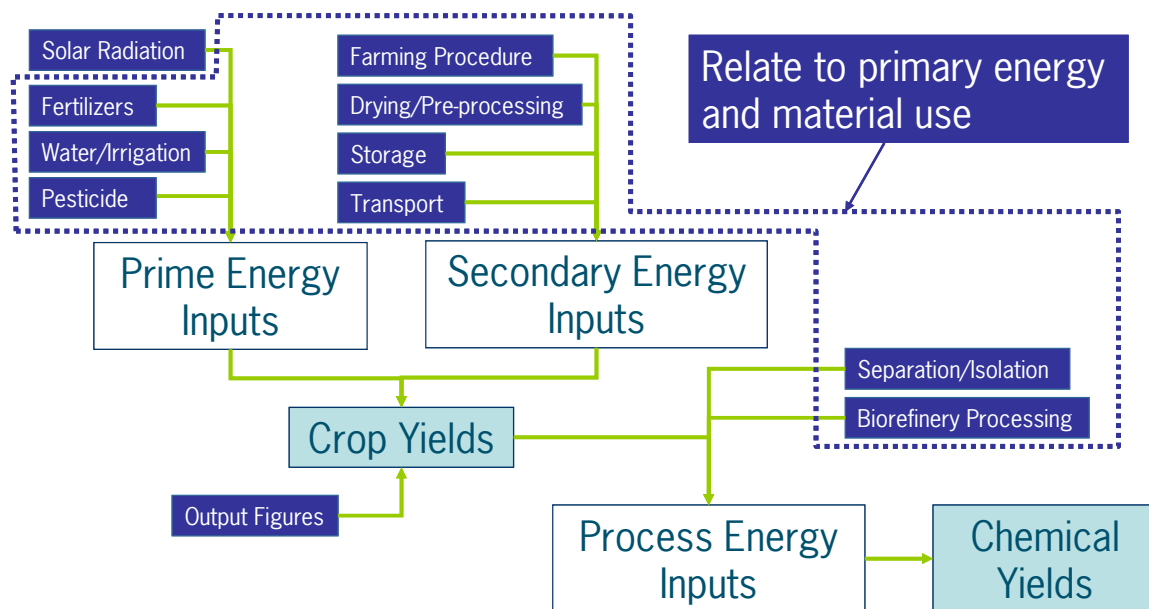

Figure 1   Simplified System Boundary for Biorefineries

Biomass feedstocks can be successfully cultivated in nearly any corner of the globe. Data behind each input category is thus regionally based, dependent on the biomass crop selection and corresponding location of propagation. Inventory data accumulation has a general lean towards the major producers and industries. Furthermore, a shift from standard LCI databases to independently investigate state-of-the-art technology and recent developments has been made to best predict near future trends[14]. Of which, the investigation is mainly directed at the horizontal process steps and operation energy; production of *certain* machinery, installation maintenance, managerial systems, and several other minor indirect process streams are considered outside the boundary. *All* materials involved in the horizontal processing path are back tracked into their initial fossil energy input.

1.2.4   Impact Assessment

1.2.4.1   Calorific Value

Bioenergy like biogas and biofuel like bioethanol are used to offset the calorific value of the fossil product they displace; for biogas natural gas and for bioethanol gasoline. The calorific values and efficiencies within their intended application are different than for the traditional fossil product. These differences must be taken into account when comparing the biomass product categories bioenergy and biofuels.

> Consider[15-17]: The calorific value of Groningen natural gas is 38.0GJ/ton and a large modern gas turbine has an energetic efficiency of 41% with 99% flame utilization, thus 39.6% or a harvestable fossil energy of 15.05GJ/ton. The calorific value of typical biogas composition is 21.0GJ/ton and while a large modern gas turbine still has an energetic efficiency of 41%, the flame utilization is 90%, thus 36.9% or a harvestable bioenergy of 7.75GJ/ton. Leading to 1ton of natural gas being displaced by 1.94ton of virgin biogas.

1.2.4.2   Cumulative Energy Consumption (CEC)

The resulting calorific value is a valuable tool to compare the products that are employed in combustion situations. Biomaterials, like plastics, are not (initially) intended for combustion but are meant to replace the production processes associated with the petrochemical industry. The cracked portion of oil (and increasingly natural gas), naphtha, is used as a feedstock with additional energy required for the reactions and processes. The cumulative energy consumption to be determined by assigning the feedstock a cost (embedded chemical energy) and tallying the process energy. Biochemicals have the potential to mitigate direct and indirect fossil fuel energy associated with the production of their petrochemical counterparts. The factory gate simplification can only be performed if the biochemical product is identical to the existing petrochemical product. Many proposed biobased chemical products are not identical but are entirely new products with unique composition and properties (e.g Dupont's Sorona/1,3PDO and Naturework's PLA). In many cases the properties of the biobased product are less desirable requiring the extension of the assessment beyond the factory gate to the grave. Little enthusiasm from both consumers and industrialists exist towards these new and often inferior products tagged with a green label; biobased chemicals should be present in the current petrochemical array. This has the benefit of using existing infrastructure, maintaining low downstream processing costs and negates the need to investigate the products beyond the factory gate stage.

1.2.4.3   Exergy

Especially in the chemical industry it is becoming increasingly common for engineers to include exergy as an efficiency parameter[18]. As opposed to solely relying on energy, exergy adds an extra dimension to the calculations that is highly useful in determining inefficient steps of a process. Energy is based on the 1st law of thermodynamics, which argues the conservation of energy. Exergy expands it by also including the 2nd law of thermodynamics, which argues the increase of entropy after each system change. Exergy is a measure of work potential contained in the energy stream and the loss after each system change. In layman terms, energy is a measure of quantity

and exergy is a measure of the quality (or ability of energy to do work). Striving for the maximum exergy efficiency will ensure that the maximum amount of work potential is utilized from the resource, herein fossil fuels. With the impending scarcity of fossil fuels, maximizing their work output is vital, especially when describing exergy requirements and efficiency of new feedstocks and process routes. Including it in the assessment will stress sections and process elements with large differences between energy and exergy, revealing opportunities to further improve efficiency. Seen from a single step, in many cases the difference between energy and exergy is minimal. Some noticeable exceptions do arise, in particular thermal transfer operations. Exergy indicates areas of future improvement and better process integration when brought into a cascade of interlinked processes.

> Consider[15, 19]: 1 ton of steam at 150°C and 4.8bar. The energy content is 3.37GJ whereas the exergy content is 0.71GJ which gives an energy to exergy ratio of 0.211. Additionally, a boiler has an energy efficiency around 85% whereas the exergy efficiency is closer to 50%. Meaning with better integration the exergy efficiency could be increased requiring less fossil fuel.
>
> Example[20]: A modern crude oil distillation cracker unit has an overall exergy efficiency of only 5.2%, suggesting a grand potential for improvement. Currently, high quality (exergy) fuel gas is used to produce middle-quality heat (300°C) with the major portion of irreversibility created through low-quality cooling requirements. By utilizing a portion of the cooling exergy for district heating or other low temperature (60°C) operations, the overall exergy efficiency can easily be increased by 16% to 6.0%.

1.2.4.4   Exergetic Cradle-to-Factory Gate

Both energy and exergy will be used as indication factors and both will follow the cradle-to-factory gate assessment methodology. Once the data has been fully compiled any stark difference between the two values, either totally or on an individual process, will reveal a far from ideal use of a resources work potential, opening future suggestions for technological development. The absolute difference between the total fossil exergy inputs of the biorefinery route compared to the petrochemical route represents the degree of sustainability and will more reliably indicate the overall fossil fuel mitigation potential than energy alone[*].

1.3   New Process Chains

1.3.1   *Crop Choice and Crop Data*

In the field of biomass several crops are topical and convey the hopes of the biobased economy. Fast growing, high yielding, and low input with a high degree of familiarity are the criteria employed in the selection. Also to consider in the feedstock selection are different crop types such as oil-rich, starch-rich, sugar-rich, cellulose-rich, etc. This results in a moderate variety of crops species in areas common for their cultivation. Aside from the natural deviation between the cultivation years deviations exist between agricultural practices. Averages listed for any region include all farmers good and bad, large-scale and small-scale, industrial minded and eco-minded,

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[*] *Detailed description and overview of calculations in accompanying WUR document: Chemical Biorefinery Perspectives*

etc. Experimental farm plots indicate the highest obtainable yields under optimally controlled conditions. Realistic biomass yields, included in this study, pertain to the upper boundary of typical farms, basically best practice. In the near future, when large scale biomass implementation occurs these yields should be realistic to supply biomass feedstock. The average and best practice crop yield figures are greatly dependent on the relative area of cultivation.

> Example[17, 21]: Sugar beet in the Netherlands. In 2001, the average wet beet yield was 54.96ton/ha and has consistently risen each year to 65.18ton/ha by 2005. Typical large scale farms in the central areas obtained 72.4ton/ha in 2002-2004. Yields reaching 100ton/ha are becoming common, representing best practices.

As previously mentioned, Figure 1 outlines the influence of the biomass output figures (crop yields) on the material and energy balance of the entire biorefinery concept. Albeit any crop can in principle be selected as a biomass candidate, following the desired criteria for biomass applications (e.g. high yields, low agricultural intensity) is advisable. Specific regional conditions, data, and dependencies need to be gathered upon selection of a biomass crop. The sugar beet *(Beta vulgaris L.)* in the Netherlands will be used throughout this paper as an exemplary crop providing practical figures to the described assessment methodology.

1.3.2   *Maximum Crop Utilization*

Food crops are cultivated for the edible portion, the rest is agricultural waste and is either left on the field to maintain soil fertility or used as animal fodder. The desirable portion of the sugar beet, for example, is the sucrose contained in the taproot (or beet). The tops (leaves, stems and uppermost beet section, indicated as *"above soil"* in Figure 2) and the residues of the sugar diffusion and crystallization process are not desirable in food processing and are treated as agricultural waste. Co-product utilization is low. The same crops can also be used for non-food applications.

Initial biomass schemes, which envision the use of traditional food-based crops, have focused on the same edible portion using technology based on processing starch, sugar, oil, etc. Co-product utilization remains low. Newer biomass schemes envision the use of non-food based crops and the normally considered agricultural wastes act as additional feedstocks. Full utilization of a crop grown specifically for biomass (non-food) purposes is possible. The fossil fuel energy involved in the entire agronomic operation (cultivation and harvesting) is effectively lowered. In instances where only a small portion of the crop components are utilized, the relative biomass production costs will be high, lowering the amount of potential fossil fuel replacement. Striving for a higher proportional utilization of the crop components is the first step in optimizing biomass utilization.
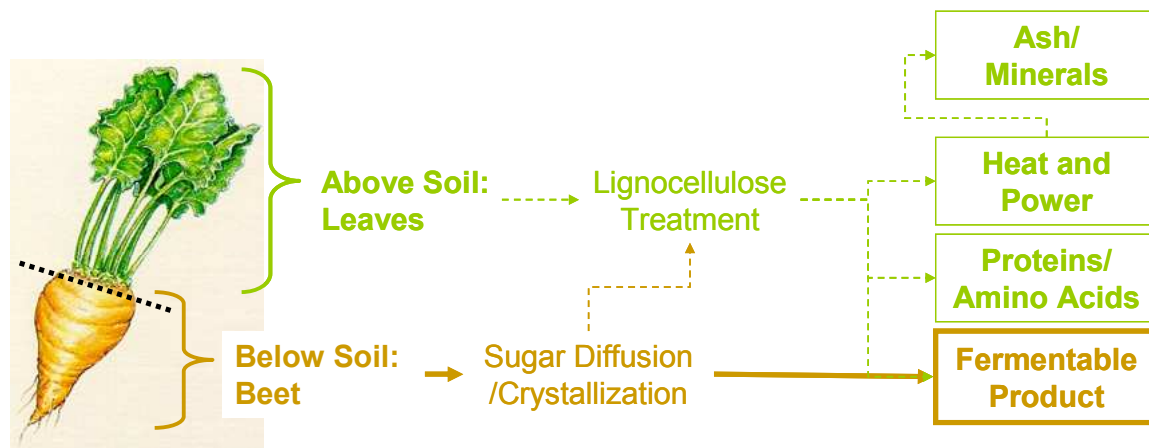
Figure 2   Crop Utilization

Figure 2 illustrates the typical and possible uses of the sugar beet components. Processing the sugar contained in the beet fraction to create fermentable products is commonly suggested as an exemplary method to produce biofuels[22]. The rest of the crop is treated as waste. Incorporating newer and recently developed technologies can allow the other components to also be converted to yield products; energy and materials.

1.3.3   New Technologies Involved

1.3.3.1   Logistics

Crop yields are almost entirely listed in wet weight terms and the moisture or water content of biomass can vary immensely, ranging anywhere from 10 – 90%; dry biomass is typically below 20% and wet biomass above 60%. Food and non-food crops are currently harvested wet and shipped directly to the processing facility; justifying expression in wet weight terms. The dry matter content determines the quantity of end products, water has no immediate product use. Water is an unnecessary weight and has a direct impact on the transportation costs and energy requirements. Wet biomass (e.g. 70%) transports more than three times the weight needed for the biomass application. Industry supplied by biomass feedstocks are rarely located in the near vicinity of plantations making transportation a major factor. A perfect example is Rotterdam, which will obtain more biomass feedstocks globally then from its hinterland. Furthermore, biomass shipped directly from the fields is solid with irregular shapes (e.g. beets are oval), meaning not only is more weight but also more volume than needed transported to supply the dry useable matter of biomass. Conducting pre-emptive processing steps (like mashing) combined with dehydration steps (like filter-pressing) will increase the net packing density of transported biomass. The amount of fossil fuel saved through the reduction in transportation easily compensates for the additional energetic inputs of the pre-processing steps, especially on long-haul voyages. Each plausible technology must be assessed and determined separately for the crop-based and regional-based logistics system.

Example[23-26]: Delivery of Dutch cultivated sugar beet to a biorefinery in Rotterdam requires an average transportation distance of roughly 225km (tractor: 5km, truck: 20km provincial roads & 200km highway). Transported wet (both beet and tops) leads to a total logistic system energy cost of 3.5GJ/ton delivered dry weight (DDW). Including near-field pre-processing (sizing and moisture reduction) involves an extra cumulative energy input of 1.0GJ/tonDDW, but results in lowering the logistics system to 1.4GJ/tonDW.

1.3.3.2 Lignocellulose Treatment

Converting the "edible" carbohydrate portions of biomass into biobased products (like ethanol) can be considered conventional technology[27]. The first step to be able to use a larger fraction of the harvested biomass is a pretreatment step, listed as *"lignocellulose treatment"* in figure 2. Without pretreatment the densely-packed and rigid crystalline cellulose structure is resistant to enzymatic hydrolysis[28]. Hydrolysis is necessary to permit fermentation of lignocellulistic material (C5 and C6 based polysaccharides) into bioproducts. Lignin will be covered later.

There exist numerous pretreatment options to better facilitate the enzymatic hydrolysis before fermentation[29]. All technologies in the lignocellulose-to-ethanol research field are still under investigation, whether on the laboratory scale or the pilot plant scale. A technology close to actual feasibility and with the lowest (calculated) energy intensity is the ammonia fast expansion (AFEX) with subsequent enzymatic hydrolysis[30, 31]. It has recently been successfully tested on corn distillers grains resulting in high conversion rates and can be expected to perform equally well on other process residues[32]. A portion of this assessment methodology was conducted to determine the internal cumulative energy of the AFEX pretreatment for several feedstocks [33]. The optimal pretreatment technology is feedstock type dependent and must be individually determined for each biomass feedstock (e.g. AFEX performs poorly on high-lignin containing feedstock). Each option must be assessed based on the total required process energy in relation to the product yields. In the example of the sugar beet, AFEX is selected as it is well suited to pretreat the process residues. In the subsequent enzymatic hydrolysis, newer enzymes (cellulases) are continually being developed that have a higher activity and promote the digestion under more energetically favourable conditions[34, 35]. Together with the specially developed fermenting micro-organisms the leaves, stems, residues from traditional food processing methods, and other agriculture wastes can be used as a feedstock. Lignocellulistic material represents the largest proportion of plant matter and with proper product utilization will greatly lower influence of the energy intensive agricultural procedures.

1.3.3.3 Protein Separation and Isolation

Leafy matter and residues from the traditional processing steps contain a moderate quantity of protein, typically ranging between 10 – 15% dry weight basis. Several crop species have plant organs (fruits and seeds) that are composed of highly concentrated protein with levels reaching above 40%, like the soybean[36]. It is possible to use solvents and other extraction methods to solubilise the protein content and isolate them using simple solid/liquid separation methods. The leaves of the sugar beet can, for example, be subjected to a slightly modified pulp milling treatment to separate the fibrous (solid) from the cytosolic and parenchyma (liquid) portion[37].

The juice contains high levels of protein and further treatment isolation and concentration is foreseeable. Protease enzymes are capable of digesting proteins into their individual amino acids. The breakdown of organic material with the help of enzymes is well-developed and mature in the detergent industry, especially in the laundry sector[38]. In regards to biomass, the field of proteases is relatively immature with optimal conditions and particular enzymes confined to the food industry. In a recent investigation, it has been proven that even food-grade proteases (developed for wheat gluten) can solubilise, digest, and break down corn proteins from biomass residues into small peptides[33]. Amino acids can further be isolated using specific techniques based on their physiochemical characteristics such as polarity, acidity or basicity of the side chains, hydropathy, etc.[39, 40]. The energy intensity of performing such separation and isolation steps cannot be overlooked, especially when extending the electric demand to the cradle. Acquiring amino acids, however, has the benefit of replacing bulk petrochemical derivatives, like the nitrogen containing chemicals that normally require substantial fossil processing energy inputs [12, 41]. Employing amino acids as feedstocks will promote the optimal use of the built-in functionality of amines, which are able to by-pass some of the most energy intensive production routes in the chemical industry, e.g. the Haber-Bosch process.

> Example[41-43]: 1,4-Butandiamine has a cumulative energy value of 114.7GJ/ton. Through an enzymatic hydrolysis and decarboxylation it can also be produced via the amino acid arginine. Following the stoichiometric ratio, 0.459kg is yielded as a maximum per 1kg of aspartic acid. The associated bioprocessing costs can reach as high as 52.6GJ/ton (minus the embedded agricultural input) before costing more fossil energy than mitigated. Preliminary internal calculation place it at around 30.7GJ/ton.

Several studies and reports have been compiled to determine the internal energy and exergy loss of chemicals processes[44]. These are effective at determining the internal inefficiencies of the processes but cannot determine the current cumulative exergy consumption of the processes. Exergy must be related to the original fossil fuel input. The amount of cumulative exergy (and energy) required to manufacture chemicals from protein contained in biomass feedstocks is considerable but significantly less than the maximum allowable for mitigation. Biomass-derived proteins for amine chemical production are still in their paper hypothesis and initial laboratory experimental phases, however their utilization does have a large potential to contribute to the best biorefinery layout in retrospect to fossil energy mitigation. This warrants their research and study direction. An example of the calculated cumulative process energy and exergy consumption can described for a foreseen amino acid isolation technology:

> Electrodialysis (ED): 153kWh/m³ permeate is required to partially isolate amino acids. Electricity represents 80%, thus 119.7kWh/m³. Originating from a natural gas turbine with an overall energy efficiency of 39.6%, 302.3kWh/m³ energy is needed. As natural gas has a 1:1 chemical energy to exergy ratio, it is the same exergy quantity. The other 20% is from using low pressure steam (115°C/1.6bar) to heat the permeate. Low pressure steam has an energy/exergy ratio of 0.099. Originating from a fuel oil burner that has an overall energy efficiency of 80%, 42.3kWh/m³ energy is needed. The exergy efficiency is 50% and fuel oil has a 1:1.07 chemical energy to exergy ratio, resulting in 7.2kWh/m³. At 6.5g amino acid per ton permeate the CEC is 19.1GJ/ton and the CExC is 17.1GJ/ton.

1.3.3.4   Combined Heat and Power Unit with Ash Collection

A consequence of incorporating all the above bioprocessing steps together is the accumulation of one final wet material stream. Composing partly of the unconverted components, the primary composition of the waste stream is lignin (soluble and insoluble), ash, and process water. Several product propositions have been investigated for lignin but have thus far proved immensely difficult especially when originating from impure sources[45]. Burning the waste stream to harness the calorific value is a common and viable option. In many single-product biorefinery layout schemes burning the residual stream (largely lignin) provides enough process energy to cover the entire internal energy demands and yield excess electricity is supplied to the grid[34]. In the assessed biorefinery concepts it is related to the final product mix (functional unit), requiring a tailored mass allocation for each biorefinery system. The difference between energy and exergy cannot be starker than in the combined heat and power unit (CHP).

> Example[15, 19, 34]:   The residual waste stream contains 17.5GJ/ton energy and 19.0GJ/ton exergy based on the composition. The first step is drying, which depending on moisture content can cost between 1 to 4GJ/ton for pressing and evaporation. At 70% moisture, 2.5GJ/ton steam energy (or 0.53GJ/ton exergy) can be expected. The efficiency of a new CHP unit is 85% energy and 45% in exergy terms. The resulting combustion energy is 12.4GJ/ton and 8.0GJ/ton exergy.

Except for the exported electricity, burning lignin and other components contained in the waste stream does not yield a material product, meaning there is no allocation of the agricultural input energy. Collection and redistribution of ash to the agricultural lands, conversely, mitigate the need for certain synthetic fertilizers, meaning a minimal reduction in allocating the agricultural input energy requirements. In fact, aside from nitrogen all the nutrients applied to a biomass crop will end up, though in their oxidized form, as ash [46].

1.4   The Pictorial Guide

1.4.1   Bioenergy

Bioenergy is based on the potential output energy released through combustion. The initial calorific value, type of combustion unit, and the associated boiler/burner efficiency must be taken into account. Exergy investigates the type of energy being produced independently; treating heat, steam, and electricity separately. Combined the values represent the fossil exergy of the grid mitigated. As the entire crop is treated as a feedstock and subjected to the processing for combustion the agricultural allocation is 1:1 for all the biochemical components used. This maintains a minimum input of feedstock, as long as the agricultural intensity of the selected biomass crop is also low. Figure 3 illustrates the exergetic system using the sugar beet as an example crop:
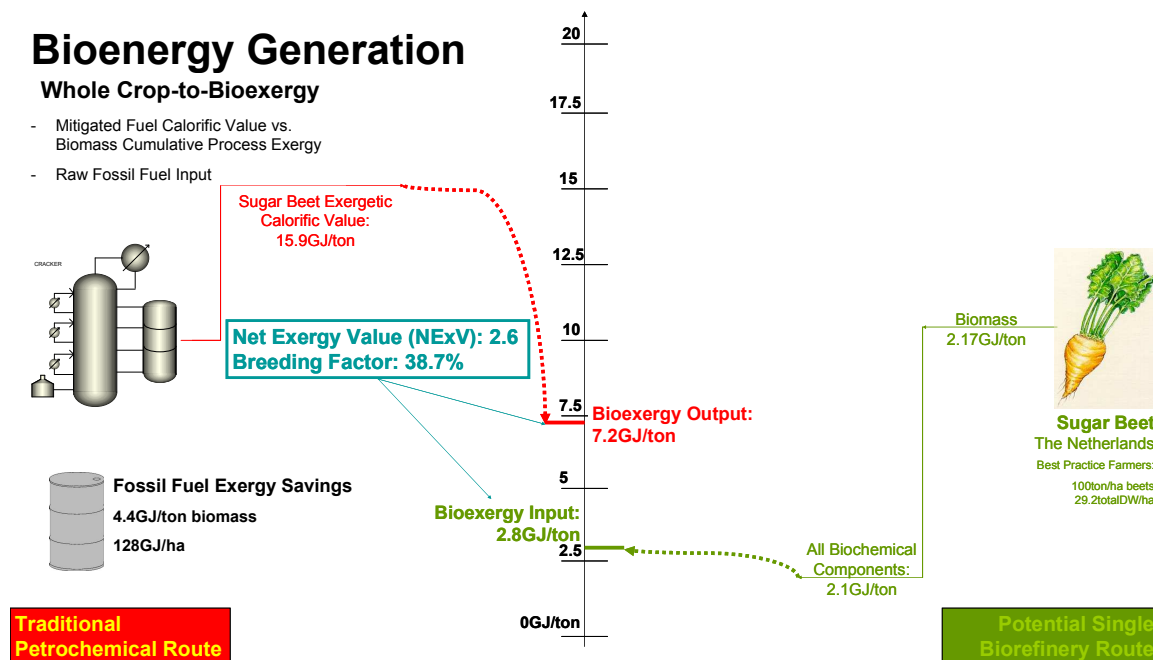
Figure 3   Pictorial Representation of Bioenergy
   - Agronomical data is based on a collection of data and estimates[36, 47-52]
   - Sugar processing based on a portion of the sugar milling and drying[53]

Beneath the image of the biomass crop (here the sugar beet) on the right hand side is the regional best practice biomass yields of the crop (in this case the Netherlands). The exergetic value is a summation of the agricultural costs according to Figure 1 in terms of GJ per ton dry weight. It will be from hereon referred to as *"total biomass agricultural exergy intensity value"*. The green dotted line connected to *"bioexergy input"* represents the processing exergy requirements to prepare the biomass for combustion; understood as size and moisture reduction. On the left hand side is an image of an oil cracker used to symbolise the fossil exergy mitigation potential. For bioenergy purposes the lower heating value is the starting point, however the *"bioexergy output"* is taken into account which is based on the overall combustion efficiency. This is represented by the dotted line (15.9 → 7.2). The resulting yielded output versus the total input is used to calculate the net exergy value (NExV) and breeding factor. Alongside the oil barrel image is the *"fossil fuel exergy savings"*, in *"GJ/ton biomass"* which indicates how much fossil exergy is saved per ton of dry feedstock and the *"GJ/ha"* which indicates how much fossil exergy is saved per arable land area.

1.4.2   Biofuels

1.4.2.1   1st Generation

1st generation biofuels are understood as bioethanol and biodiesel created from the traditionally edible portion of biomass crops; simple carbohydrates (like starch and sucrose) and fatty acids (oils), respectively. They have received the name 1st generation as they denote early attempts at developing biofuels from biomass. Large portions of the crop are not utilized; portions left on

the field as waste or other process residues marketed as low-grade animal feed. The allocation of the agricultural intensity is best illustrated in the following illustration (Figure 4):
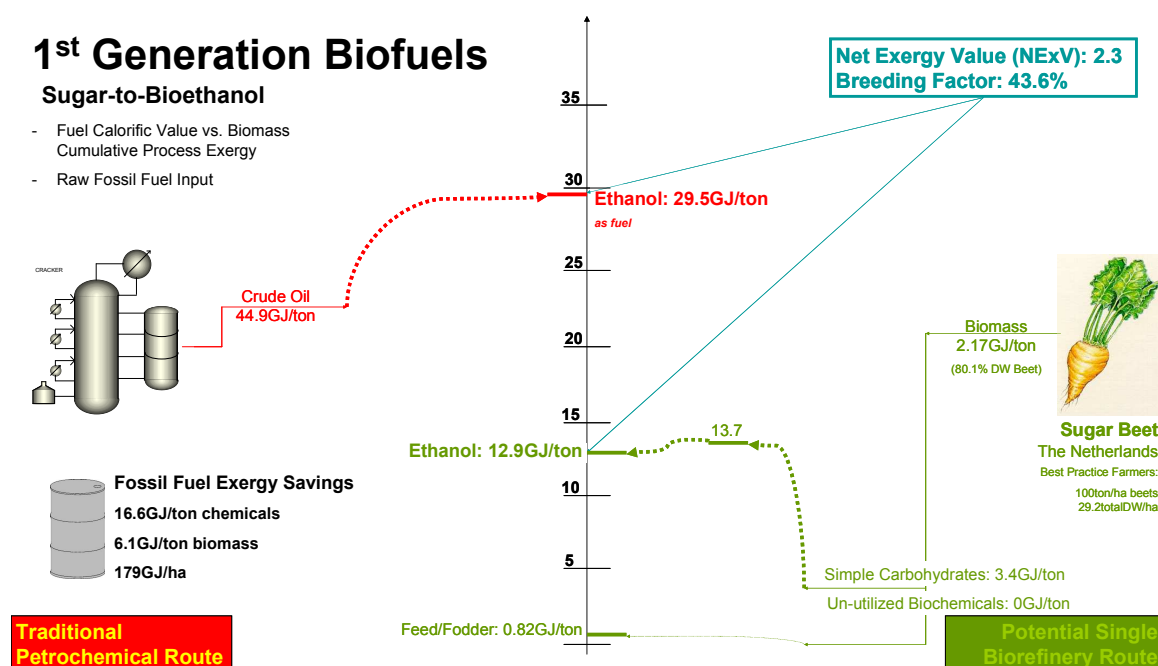

Figure 4   Pictorial Representation of 1st Generation Biofuels
- Sugar processing based on typical sugar milling and ethanol producers[27, 54]
- Sugar to ethanol conversion figures based on current ethanol industry[34]
- Feed/fodder energy costs based on soy bean production and relative protein content[55]

Directly under the total biomass agricultural exergy intensity value is the dry weight ratio of the beet. The above soil portion is not used in this layout, allocating the costs fully to the beet portion. Sucrose and other free sugars (above: simple carbohydrates) are the only constitutes processed into the bioproduct (ethanol). As they represent only a portion of the beet, the allocation of the agricultural exergy is set solely for that biochemical group. The process exergy required to convert simple carbohydrates to ethanol is indicated by the dotted green line; conversion rates and yields are considered. The *"un-utilized biochemicals"* are not assigned a portion of the allocated biomass agricultural exergy intensity because they do not contribute to the production of a chemical product. In this biorefinery layout, residual streams are used as low-grade animal feed, which has the potential to mitigate a portion of the fodder industry. A common fodder is soy bean meal, employed for its high protein content (around 45%), the difference in protein concentration and quantity is used to determine the amount of fodder mitigated. It amounts to the fossil exergy inputs attributed to fodder preparation. The resulting bioproduct (fodder) value is expressed on the graph as GJ per ton (ethanol) and is subtracted from the intermediary processing figure (here 13.7) to obtain the resulting cumulative input exergy. As with the bioenergy graph an oil cracker is depicted with the calorific value of crude oil and the connecting ling represents the actual calorific value of the biofuel (ethanol). For systematic display the various forms of resulting fossil exergy savings calculations are included.

The *"GJ/ton chemicals"* has been added to signify the amount of fossil exergy saved per ton of bioproduct.

1.4.2.2 2nd Generation

As the name suggests 2nd generation biofuel production incorporates newer techniques that facilitate a higher proportion of biomass conversion, namely the lignocellulose constituent. The sugar-to-bioethanol production route as described in the 1st generation is still employed; additionally the waste and above soil portion are used as a feedstock for the lignocellulose-to-bioethanol production route. Combined the proportion of biomass included as a feedstock source is higher. This beneficial effect can be seen in Figure 5:
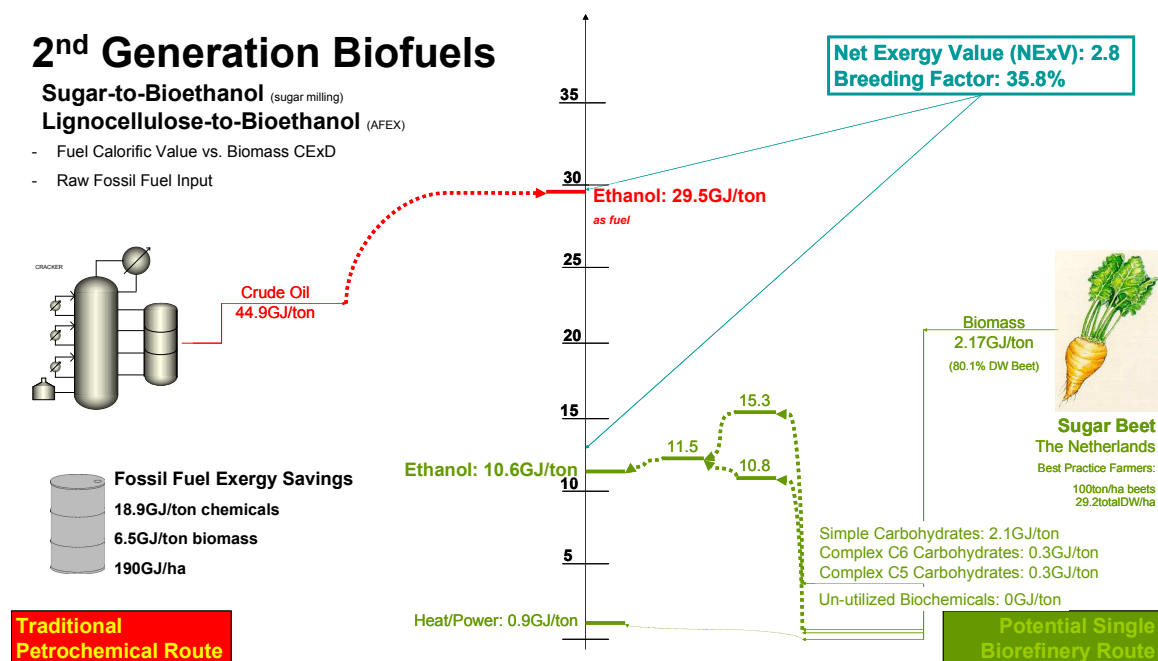

Figure 5   Pictorial Representation of 2nd Generation Biofuels
  - Lignocellulose to ethanol conversion figures based on current state-of-the-art[31, 32, 56]
  - Biomass combined heat and power efficiency based on residual combustion[15, 18, 57]

Compared to the 1st generation technology there are 3 as opposed to only 1 component used as feedstocks; plus the tops/leaves also contribute to increase the feedstock quantity. This has a noticeable effect on the allocated agricultural exergy input as seen by the significantly lowered values of the carbohydrates. The other components are again displayed as *"un-utilized biochemicals"* and treated as waste with no associated agricultural cost. In the 2nd generation system, they are all subjected to combustion in a CHP. The yielded exergetic output *"boiler"* is expressed in GJ per ton product and subtracted from the intermediary processing figure (ethanol).

1.4.2.3 Chemical Biorefinery

Maximizing the proportion of biomass utilized in the production of products is the first step in achieving a successful biorefinery system. The following (Figure 6) pictorial guide highlights a straightforward early chemical biorefinery concept for three grouped product types:
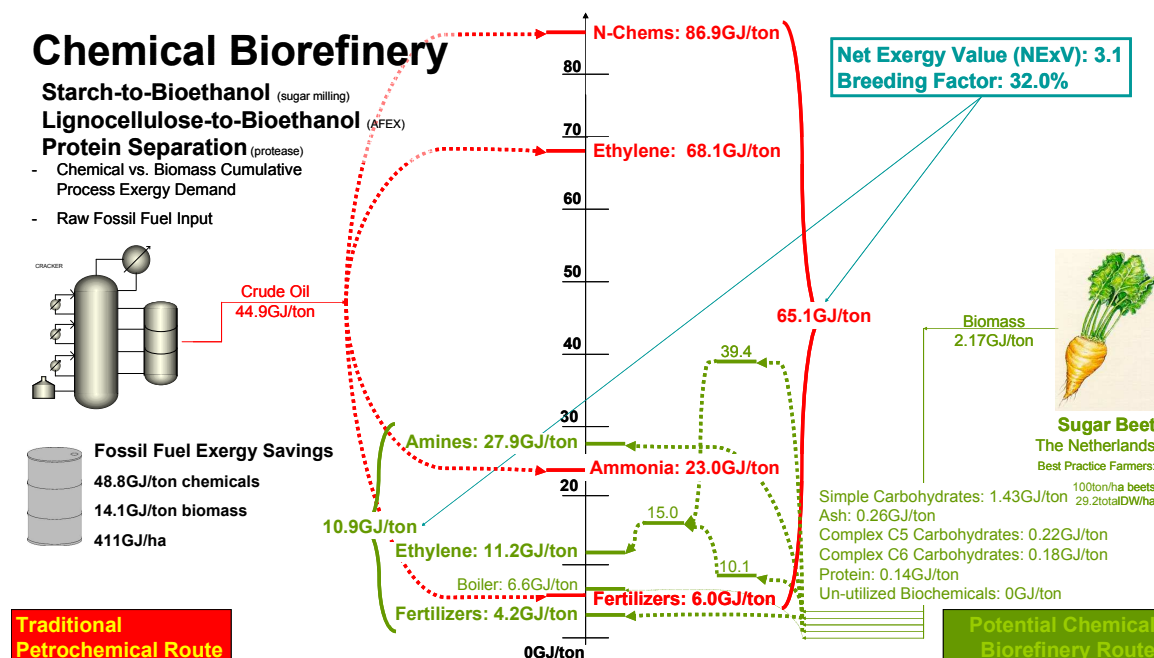

Figure 6   Pictorial Representation of Chemical Biorefinery
  - Ethanol to ethylene yield of 0.609kg/kg and 4.8GJ/ton cumulative exergy based on process parameters[58, 59]
  - Amines representative of typical amino acid distribution to produce an assortment of nitrogen-based chemicals *"N-chems"*
  - Amine bioprocessing costs based on protease experiments and internal estimates on reaction exergy costs (3 – 30GJ/ton)[33]

Despite the complex appearance, the graph follows the same basic structure as with the previous pictorial guides. In this layout, protein and ash are also included for the production of bioproducts. A total of 79% of the biomass is utilized which results in a further lowering of the allocated agricultural input energy. Proteins are used for amine chemistry to replace nitrogen containing chemicals. Each amino acid will follow similar, yet unique production paths yielding an array of nitrogen containing chemicals. These potential amine-based chemical product adheres to their own stoichiometric conversion yields and process exergy. Decarboxylation is common reaction contributing to material losses in the form of carbon dioxide. Suspected isolation and reaction exergy demand range between 3 – 35GJ/ton depending on the exact chemical reaction, conversion rate and initial amino acid concentration (biomass dependency). This is a conservative calculation assumption as it is foreseen that continued improvements in the biotechnology field should significantly reduce these processing exergy costs. Indicated by *"Amines"* in the figure, the dotted line groups (as there are 20 separate products) the total processing input for separation, isolation, and reactions. After combustion the residual ash stream of is utilized to displaces fertilizers, which includes an associated exergy input for collection and preparation. Through a simple dehydration step ethanol can be used as a source of ethylene, a material product with a

higher cumulative exergy input consumption than the calorific value of ethanol (68.1 vs. 29.5GJ/ton). The left-hand lines and values represent the total cumulative exergy consumption of the petrochemical route. The proportional product yields resulting from the biorefinery are used to calculate the total input exergy and that of the corresponding petrochemicals mix (indicated by the parenthesis). For the presented sugar beet example, ethylene embodies the bulk of the production as can be seen by the lean towards the total biomass and petrochemical input to the respective ethylene values. The exact biorefinery chemical distribution is directly correlated to the biomass feedstock chemical composition and will influence the replacement potential.

1.5 Results and Discussion

Biomass has the potential to replace many if not all aspects of the broad energy sector. It is regarded as sustainable, renewable, CO_2 neutral, and as a *"green"* alternative to current fossil fuels. However, each of the different biomass applications embody input energy composed almost entirely of a fossil nature, meaning it is only partially sustainable, renewable and CO_2 neutral. The shear level of available information and computing power allows for detailed calculations models to determine the optimal utilization option for biomass. An exergetic cradle-to-factory gate assessment as outlined herein is one such calculation model that can indicate the options with the least amount of embodied fossil fuels and the maximum replacement potential. Plus the advent of computer simulations facilitates future production options to be assessed before a plant is built, let alone conceived. In the field of biomass utilization, the single most important factor should be the level of fossil fuel energy mitigated. These levels are presented Table 1 for the Dutch sugar beet as an example for the main biomass application categories. The most logical impact assessment is the fossil fuel mitigated per arable land area (GJ/ha). All the biomass options contribute to a reduction, but the chemical biorefinery route, although not producing a combustible product, potentially mitigate the most fossil fuels. At 411GJ/ha that relates to more than 67 barrels of oil saved per hectare of arable land. While each biomass crop in each distinct region will yield different replacement potentials, the relationship between the different biomass utilization categories will consistently reveal the same beneficial trend of chemical biorefineries.

Table 1 Fossil Fuel Replacement for the Various Biorefinery Layouts.

Biorefinery Layout Examples	GJ/ton Biomass		GJ/ha Land	
	Energy	Exergy	Energy	Exergy
Bioenergy	7.1	4.4	209	128
1st Generation	3.7	6.1	107	179
2nd Generation	4.9	6.5	143	190
Chemical Biorefinery	10.3	14.1	302	411

- Current values are partly based on assumptions, estimations and hypotheses, an error of at least ±20% is expected.

The advantage of extending the assessment to include exergy is best described with the bioenergy example; between the two resulting figures a drop of 38.5% exists for exergy over energy, caused primarily by the inherent efficiency difference of the boiler. This implies that bioenergy propagation is a mature with little improvement foreseeable based on existing technology. Throughout the other process chains exergy is a valuable addition to the energy analysis to help

indicate potential improvement options to maximize the reduction in fossil fuel intensity. An increase of 26.5% in exergy terms over energy for the chemical biorefinery signals that the technology is undeveloped with a moderate potential of improvement. Vast quantities of arable land will undoubtedly be required for large-scale implementation of biomass, thus in relation to the food versus fuel debate obtaining the highest reduction in fossil fuels per arable land use indicate the best possible use of biomass. Following these arguments designates the chemical biorefinery as the most sustainable option and as the optimum utilization of biomass.

The proposed chemical biorefinery does *not* yet exist and is purely hypothetical based on existing and emerging technology, but does however indicate the benefits of thoroughly assessing the process chains. Further improvements are foreseeable with better technology and optimization of the layout as indicated by the exergy trends. The described methodology was created as a tool to indicate the future developmental path of biorefineries. The results validate the research and development direction of pursuing solutions for all components of biomass with a focus on petrochemical products. One of the reasons that the chemical biorefinery replaces more fossil fuels than the biofuel options is it utilizes a higher proportion of the biomass feedstock. The maxim for the biomass industry must be *"using the full barrel of biomass"*. Biorefineries producing biofuels also have the potential to replace higher levels of fossil fuels as more biomass is utilized, i.e. 1st generation versus 2nd generation. Biomass is and will remain local meaning strenuous investigation must be performed for each crop alongside its regional considerations. Holistic life cycle assessments, such as the described exergetic cradle-to-factory gate analysis, provide such insight and take into account such interdependencies. Only via proper assessment can the optimal biorefinery concept for each specific biomass cropping system be determined.

1.6   Conclusion

There are countless renewable energy technologies currently under investigation to replace our society's ever increasing dependence on fossil fuels. Biomass is one option that has the potential to alleviate this problem but opposed to other renewable alternatives it has a unique and beneficial characteristic; the ability to bond carbon molecules together into carbohydrates and other biochemicals. None of the other alternatives can achieve this, effectively rendering biomass the only true candidate to replace the petrochemical industry. But biomass is envisioned to cover the entire scope of the fossil fuel-based energy sector, dubbed as the biobased economy. Each of these application options (biomass cultivation routes and biorefinery layouts) do not contribute to the same replacement potential. Employing life cycle thinking is necessary to determine the level of sustainability (or embedded fossil fuel) by various biomass options. Using the described exergetic cradle-to-grave assessment has indicated that the most sustainable layout for biomass is the chemical biorefinery. Incorporating cumulative exergy consumption into the equation has also shown that the level of potential energy efficiency improvements is still large. This validates research and development efforts into chemical applications of biomass, for in the entire field of renewable alternatives the final goal is to reduce the non-renewable energy component.

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Chapter 2

Energetic and exergetic life cycle analysis to explain the hidden
costs and effects of current sulphur utilization

2

Abstract

Typical life cycle analyses of the fertilizer industry use averages based, in many cases, on outdated technology. Sulphur is a major chemical in the industry, emerging as a primary nutrient on its own accord and as a feed for other fertilizer production, namely phosphoric acid. Recent developments sparked by governmental regulation and fossil fuel processing have raised the validity of an assumption frequently overlooked. Sulphuric compounds coming from the desulphurization of fossil fuels are not to be assigned a zero energy charge as stated by many but originating from Mudahar (1987). By applying the principles of an exergetic cradle-to-factory gate analysis it will be proven that current trends will force the sulphur to acquire a feedstock cost. How this is linked with the current development of the fertilizer industry (i.e. phosphorous) is also elaborated upon.

Keywords

LCA, Life Cycle Assessment, exergy, phosphorous, fertilizer, sulphur, desulphurization

2.1 Introduction

Sulphur is such an abundant resource that it is frequently regarded as a by-product or even as a waste stream. It has become common practice to associate any costs attributed to sulphur production to the main product and not sulphur itself: *"For recovered sulphur whether energy is involved in recovering the sulphur in a saleable form is charged to the main product (natural gas or oil) so the sulphur receive zero energy charge"*[2] This statement only holds true for the recovered sulphur production methods and not for ore extraction methods, like the Frasch process. However, currently 98% of the worlds sulphur production is supplied by recovery methods and a vast majority of that is from oil and natural gas desulphurization[3] (see Figure 1).
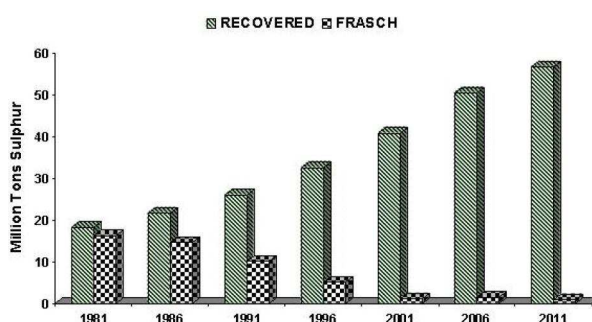

Figure 1   World Elemental Sulphur Production by Type[4]
   - Recovered: all forms of recovered and recycled sulphur excluding the Frasch process

Worldwide over 25% of elemental sulphur originates from the desulphurization of fossil fuels and alone in Europe it is already 38.6%[5]. Over the last two decades the origin of sulphur production has metamorphosed from a mining oriented industry to a co-product of the petroleum industry. Although by-product recovery from other metallic ore (pyrites) still constitute the single largest source of sulphur production, its market share is falling as recovered sulphur from fossil fuels are continuing to rise.

There is one major event in the last ten years that has shaped this development of the sulphur industry most; clean air acts. Over the last 30 years great lengths have gone into processes to reduce the sulphur content of fossil fuels and the SO_x of exhaust gases. Transport fuels above all, employ modern absorption techniques (Claus Process) to remove large levels of hydrogen sulphide, H_2S. In the last ten years, environmental policies have exponentially reduced the allowable level of sulphur in fuels (as depicted in adjacent graph) from more than 3000ppm before 1996 to around 10ppm by 2008 (see Figure 2). In regards to the fertilizer industry this has presented two major consequences.
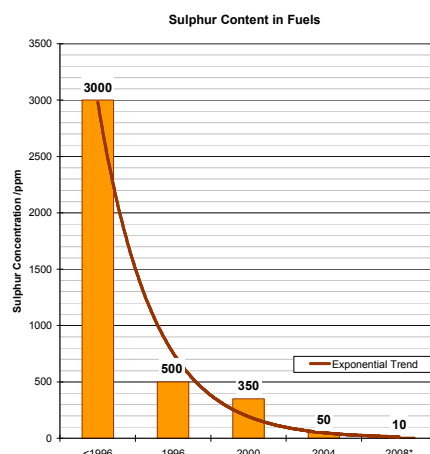
Figure 2   Sulphur Content Fuels
- 2008: Planned

2.1.1   *First Consequence*

Combustion of sulphur and sulphur containing compounds is a very undesirable process as the resulting SO_x is responsible for photochemical smog and acid rain. The various clean air acts have indeed lowered the atmospheric levels of sulphur oxides and the associated environmental pollution. However, two of the three primary mechanisms for plant life to utilize sulphur as a nutrient are directly related to the emissions of industry and the transport sector. Leaves are able to absorb SO_2 from the air and the roots are able to absorb the SO_3 constituent of acid rain. Until relatively recent times, agricultural soils have received sufficient sulphur from the deposition in air and soil from such sources. Now due to the reduction of SO_x emissions, sulphur deficiencies are becoming apparent for the first time since the industrial revolution[6]. Previously little attention was paid to the issue of sulphur; it was free, abundant and in the air.

2.1.2   *Second Consequence*

Solving the sulphur deficiency in plants is easily solved by the application of artificial fertilizers. But along side the reduction of emission-based sulphur, the fertilizer industry is also shifting away from sulphur containing compound fertilizers, like ammonium-sulphate. These two factors combined effectively mean that more sulphurous fertilizers need to be applied to the fields. Artificial sulphur nutrient application rates already represent roughly 10% the level of nitrogenous fertilizers. It is quickly being considered as the 4th macronutrient and regarded as a primary nutrient even though it is classically a secondary nutrient[7]. The growth of sulphur fertilizer operating rates is one of the main reasons why market prices are currently unstable: *"In the third quarter of this year, sulphur prices increased for the seventh consecutive quarter"*[8]. So, even as a free commodity, the pricing of sulphur and related products are becoming costly, rising from the $10/L range to over $40/L over the last 6 years[9]

Total production of sulphur in 2002 was 59Mton, yet sulphur containing fertilizers only accounted for 10Mton[10]. The bulk of the fertilizer related sulphur production is in the form of

sulphuric acid for the production of phosphoric acid, at 27Mton. So 62.7% of sulphur production is coupled with the fertilizer industry and can be expected to rise as the need for sulphur containing fertilizers increases. Phosphorus, on the other hand, is the second most utilized fertilizer in the industry and is adversely related to the cost of sulphur production. With the current notion that sulphur is free, the price of phosphorus fertilizers is also kept low or lower than they should be. Seen energetically several calculations even suggest a net process energy gain.

2.1.3   Aim of the Paper

The biobased economy is becoming a hot topic and is generally regarded as reaching large-scale implementation in the near future. Net Energy Value (NEV), or the amount of input energy versus output energy, is a widely used indicator for the biomass sector. As the nature of this work is to argue the near future energy requirements for biomass implementation, the best available technology was chosen for each of the processes. They will presumably become standard practices, basically representative of when biomass is expected to be heavily implemented. Using an exergetic limited life cycle assessment the aim is to show the differences between sulphur as a free and as a non-free energy source for the sulphurous and the phosphorous fertilizers. These calculations will explain why sulphur cannot be considered free and how it affects the fertilizer/biomass industry.

2.2   Methodology

2.2.1   Goal and Scope

The standard methodology of the ISO14040 series has been followed to a great extent with the exception that only the major material streams, energy and exergy values were documented and no environmental considerations were made. This is done because only the resulting process energy and exergy are of interest in the analysis to justify the feedstock cost. Furthermore, the cradle is set at the point of sulphur-based compound extraction from fossil fuels and the grave is set as the factory gate for sulphuric acid and superphosphate production, respectively. The boundary is affectively confined to the process. This particular LCA technique is called an exergetic life cycle assessment (or E-LCA), but is in essence a limited exergetic cradle-to-factory gate assessment as environmental considerations are intentionally omitted.

2.2.2   Data

A simplified material process flow diagram of the process is to be considered (see Figure 3).
The process data for each production step is following the best available technologies as listed:
- Hydrogen Sulphide: Hydrodesulphurization (HDS)
- Sulphur: Euroclaus process[11]
- Sulphuric Acid: Double catalysis based on sulphur burning[12]
- Phosphate Rock: Opencast dragline[13] with Moroccan rock composition[14]
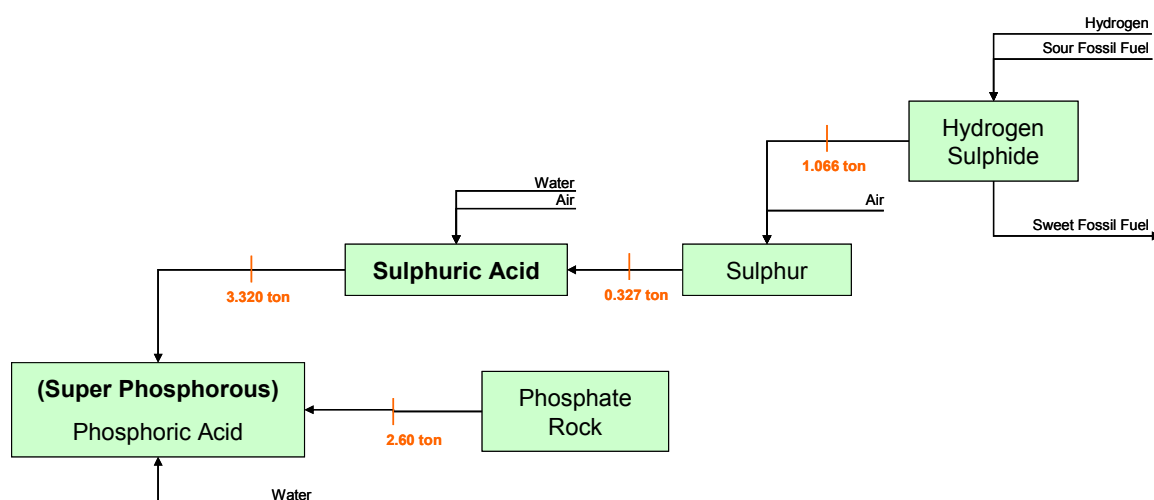- Phosphoric Acid: Hemihydrate acidulation process[15]

Figure 3   Simplified Material Process Flow Diagram

2.2.3   Impact Assessment

Both energy and exergy are chosen as the impact categories to evaluate the costs along the process chain. Exergy, the quality of energy or maximum obtainable work, is mainly included to provide further depth in the energy efficiency of the processes and as better argument against free allocation of resources.

2.3   Calculations

2.3.1   Terminology

In the case of the nutrient sulphur, the element S is not the nutritional indication figure. The industry prefers sulphur trioxide (SO_3) as this is related to the form taken up by the rooting system of crops; so all energy production figures will be calculated for the relative SO_3 content along side the absolute figures. Phosphorus is also not indicated by its elemental form, the industry prefers phosphorus pentoxide (P_2O_5) for traditional reasons as the roots take up PO_4^{-3}; so all energy production figures will be calculated for the relative P_2O_5 content along with the absolute figures. Table 1 indicates the conversion factors for the relevant chemicals.

Table 1   Nutrient Conversion Factors in w/w

$S \rightarrow SO_3$	2.497	$SO_3 \rightarrow S$	0.401
$H_2SO_4 \rightarrow SO_3$	0.816	$SO_3 \rightarrow H_2SO_4$	1.225
H_2SO_4 (78%) $\rightarrow SO_3$	0.636	$SO_3 \rightarrow H_2SO_4$ (78%)	1.571
$P \rightarrow P_2O_5$	2.291	$P_2O_5 \rightarrow P$	0.436
$Ca_3(PO_4)_2 \rightarrow P_2O_5$	0.458	$P_2O_5 \rightarrow Ca_3(PO_4)_2$	2.185
$H_3PO_4 \rightarrow P_2O_5$	0.724	$P_2O_5 \rightarrow H_3PO_4$	1.381
H_3PO_4 (52%) $\rightarrow P_2O_5$	0.376	$P_2O_5 \rightarrow H_3PO_4$ (52%)	2.656

- The nutrient conversion factors are based on the ratio between the core element in the molecule. For example:
- $H_3PO_4 \rightarrow P_2O_5$ (P is the core element)
- $H_3PO_4 = 3 \cdot 1.00974 + 1 \cdot 30.97376 + 4 \cdot 15.9994 = 97.99518$ (31.61%P)
- P_2O_5: $2 \cdot 30.97376 + 5 \cdot 15.9994 = 141.9445$ (43.64%P)
➔ H_3PO_4/P_2O_5: 31.61%P/43.64%P = 0.724
➔ P_2O_5/H_3PO_4: 43.64%P/31.61%P = 1.381

2.3.2   *Fossil Fuel Source*

Sulphur is present in natural gas and crude oil in more or less all of its organic and inorganic forms. Of the large list of possible combinations elemental sulphur, hydrogen sulphide and it closely related compounds (thiols, mercaptans, sulphides, polysulphides, etc.) comprise the majority. As a general rule of thumb quantity, stability and complexity of the compounds are greater in heavier crude oil fractions as seen in the table below. Meaning that in natural gas mainly H_2S is present where in residuum (chains above C_{20}) the whole array of sulphur compounds can be found. This will provide a challenge for oil refineries in the decades to come as the quality of crude is shifting towards a higher concentration of residuum and the trace elements associated with it, i.e. more costly crude oil. The average for recent crude oil production in Western Europe is listed in Table 2:

Table 2   Western Europe Oil Product Sulphur Content[16]

Sources	Sulphur Content (weight percent)
LPG and Naphtha	0.02
Intermediates and Blendstock	1.26
Gasoline	0.035 (today: 0.0001)
Jet Fuel and Kerosene	0.09
Diesel Fuel	0.21 (today: 0.0001)
Bunker Fuel Oil	3.1
Heavy Fuel Oil	2.2
Crude Oil, Average	1.05*

- North Sea crude oil is known for its particularly low content of sulphur; other sources are typically ranging between 2-5%.

2.3.3   *Hydrodesulphurization*

The first step in sulphur removal from fossil fuels is reacting hydrogen with the sulphur components to create hydrogen sulphide in the presence of a fraction specific catalyst. At temperatures above 300°C and pressures above 0.7MPa the reaction is brought to completion with trace quantities meeting the governmental regulated levels. The three most common reactions of the sulphur compounds found in fossil fuels are [17]:

- $RSSR' + 3H_2 \rightarrow RH + R'H + 2H_2S$
- $RSH + H_2 \rightarrow RH + H_2S$
- $RSR' + 2H_2 \rightarrow RH + R'H + H_2S$

Assumption: These can be simplified by the reaction: $S + H_2 \rightarrow H_2S$.

The reaction involves large process energies and related feedstock production costs in the form of hydrogen synthesis. It is quite logical to charge all the energy costs to the main product, the fossil fuels. However, sulphur and its components contain themselves a combustion potential. By removing them from the fuels, although the energy density is increased, the energy content is reduced. This point has been overlooked with the common assumption of charging everything to the main product. It is lost, making it free. By calculating the removed potential calorific value of the sulphur containing compounds, the residual sulphur chain is given an energy and exergy charge larger than zero, essentially giving sulphur a feedstock charge. It should not be forgotten
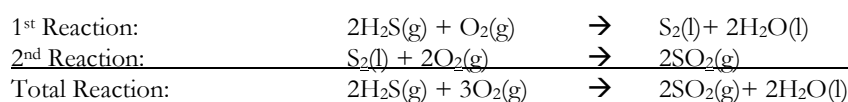
that in the lighter fractions hydrogen sulphide is naturally present and does not necessitate hydrotreating. In that case all the potential energy is allocated to the hydrogen sulphide.

Assumption: Fifty percent all the desulphurization of fossil fuels comes directly from the sulphur form H_2S

The trends in the future may look different as the quality of crude oil is decreasing whereas the fraction of natural gas production is on the raise. It could go either way. The actual sulphur levels and forms are regional based and should be determined for the adjacent sulphur/sulphuric acid plant in question.

2.3.4   Sulphur Feedstock Cost
Isolating hydrogen sulphide for combustion will release a large quantity of energy:

1st Reaction:	$2H_2S(g) + O_2(g)$	→	$S_2(l) + 2H_2O(l)$
2nd Reaction:	$S_2(l) + 2O_2(g)$	→	$2SO_2(g)$
Total Reaction:	$2H_2S(g) + 3O_2(g)$	→	$2SO_2(g) + 2H_2O(l)$

The overall heat of combustion (higher calorific value) can be calculated using Hess's Law:

Standard molar enthalpy of formation [1]

$\Delta_fH^o(H_2S) = -20.1kJ/mol$
$\Delta_fH^o(O_2) = 0kJ/mol$ (element)
$\Delta_fH^o(S_2) = 0kJ/mol$ (element)
$\Delta_fH^o(H_2O) = -285.8kJ/mol$
$\Delta_fH^o(SO_2) = -296.1kJ/mol$

$\Delta_cH^o = \Sigma\Delta_fH^o(\text{Products}) - \Sigma\Delta_fH^o(\text{Reactants})$
1st Reaction: $2\cdot(-285.8) + 1\cdot(0) - 1\cdot(0) - 2\cdot(-20.1) = -531.4$ kJ/mol
2nd Reaction: $2\cdot(-296.1) - 1\cdot(0) - 2\cdot(0) = -592.2$ kJ/mol
Total Reaction: $-443.4 + -592.2 = -1123.6$kJ/mol

$\Delta_cH^o(H_2S) = -1123.6$kJ/mol

$$HHV = \frac{\Delta_cH^o(H_2S)}{\widetilde{M}(H_2S)} = \textbf{32.97GJ/ton}$$

The heat of combustion for hydrogen sulphide and sulphur is 33.0GJ/ton and 18.5GJ/ton, respectively. Using the assumed hydrodesulphurization reaction the level of energy associated with the sulphur compounds can be found:

$H_2(g)$	+	$S(g)$	→	$H_2S(g)$
2.0159g/mol		32.065g/mol		34.081g/mol
59.1kg		940.9kg		1000kg
110.9GJ/ton		18.5GJ/ton		33.0GJ/ton
6.5GJ		**17.4GJ**		**33.0GJ**
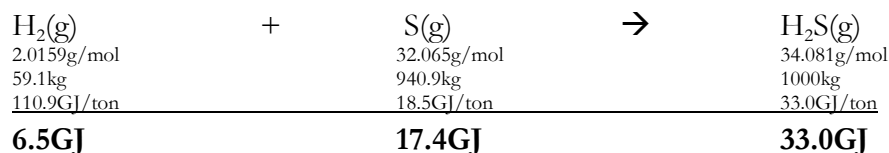
Total process (incl. feedstock) energy of hydrogen is larger than its calorific value; following a modern Syngas production installation roughly 170GJ of natural gas is required per ton of hydrogen. This difference of 65% additional energy will not be included in the calculation as it is, rightful so, allocated to the main product. Also the process energy required to drive the reaction is allocated to the main product. However, of the resulting 33.0GJ, 17.4GJ (or 52.8%) is related to the sulphur contained in the fuel. By adjusting the hydrogen sulphide composition from 0 to

100% for the sulphur naturally occurring in fossil fuels the overall energy content of sulphur lays in the range between 17.4 and 33.0GJ/ton. Following the 50% assumption it is **25.2GJ/ton**. That is a stark contrast to the commonly assumed zero.

2.3.5   *Process Energy Costs*

The following tables (see Table 3 – 8) outline the resulting processing figures for the entire chain with a sulphur feedstock energy content of 25.2GJ/ton and according to the processes listed in the methodology. The steam calculations are based on the relationship between enthalpy, pressure and mass flows following steam charts[18]. Cumulative calculations represent the sum of all the preceding processes and feedstock energy inputs to the point of determination. Cumulative electrical production efficiency, for instance, is set to 45%.

Table 3   Liquid Sulphur Processing Figures

	Component	Symbol	Use	Quantity	Unit
Input	Hydrogen Sulphide	H_2S	Sulphur Source	1.066 (26.9)	ton (GJ)
	Dry Air	Air	Oxidation Source	2.162	ton
	Electricity	kWh	Utilities	52.8 (0.42)	kWh (GJ)
Output	Sulphur	S_2	Intermediate	1	ton
	Steam (0.8MPa)	H_2O	Export (Excess)	0.370 (1.30)	ton (GJ)
	Steam (4.0MPa)	H_2O	Export, Power	2.23 (8.70)	ton (GJ)

➔ Total process energy: 17.28 GJ/ton S_2

Table 4   Sulphuric Acid Processing Figures

	Component	Symbol	Use	Quantity	Unit
Input	Sulphur	S_2	Sulphur Source	0.327	ton
	Dry Air	Air	Oxidation Source	7.795	ton
	Water	H_2O	Hydrogen Source	0.555	ton
	Water	H_2O	Dilution Source	1.190	ton
Output	Sulphuric Acid	H_2SO_4	Intermediate	2.19*	ton
	Steam (1.10MPa)	H_2O	Export (Excess)	0.720 (2.51)	ton (GJ)

- the mass balances are based on 1ton of 100% sulphuric acid concentration; a water stream is added to bring it to its final 78% concentration causing a mass dilution ratio of 45.6%.

➔ Total process energy: -1.15 GJ/ton H_2SO_4 (78%)

Table 5   Resulting Energy Requirements for Sulphur Fertilizers

Compound	Process Energy GJ/ton	Cumulative Energy GJ/ton	Sulphate Content %	Relative Nutrient Energy GJ/tonSO₃
Sulphur	17.28	17.28	250	6.91
Sulphuric Acid	-1.15	1.442	63.6*	2.27

- Dilution to 78%H_2SO_4

➔ Total energy cost: 2.27GJ/tonSO₃

Table 6   Phosphate Rock Processing Figures

	Component	Symbol	Use	Quantity	Unit
Input		P_2O_5		0.334	ton
		CaO		0.506	ton
	Phosphate Rock	SiO_2	Phosphorus	0.019	ton
		F	Source	0.040	ton
		CO_2		0.045	ton
		Other		0.056	ton
	Electricity	kWh	Utilities	107.5 (0.86)	kWh (GJ)
	Water	H_2O	Various	5.678*	ton
Output	Phosphate Rock	$Ca_3(PO_4)_2$	Intermediate	1	ton

- The water usage in the mining industry is notably high; however recent recycling initiatives have reached rates above 88%, so the actual fresh water consumption is closer to 0.680ton.

→ Total process energy: 0.86 GJ/ton $Ca_3(PO_4)_2$

Table 7   Phosphoric Acid Processing Figures

	Component	Symbol	Use	Quantity	Unit
Input	Phosphate Rock	$Ca_3(PO_4)_2$	Phosphorus Source	2.600	ton
	Sulphuric Acid	H_2SO_4	Reactant	3.320	ton
	Electricity	kWh	Crushing, Utilities	120 (0.96)	kWh (GJ)
	Water	H_2O	Dilution	0.770	ton
Output	Phosphoric Acid	H_3PO_4	Intermediate, Fertilizer	2.656*	ton
	Phosphogypsum	$CaSO_4$	Waste	4.800	ton
	Fluosilicic Acid	H_2SiF_6	Waste	0.020	ton

- The mass balances are based on a 52%mass P_2O_5 relative concentration; 2656kg of phosphoric acid contains 1 ton of P_2O_5. This is the commercial concentration for phosphoric acid for use in downstream fertilizer production, namely NPK. Virgin phosphoric acid can also be used as a fertilizer and is nearly identical to triple-superphosphorous (TSP).

→ Total process energy: 0.96 GJ/ton P_2O_5

Table 8   Resulting Energy Requirements for Phosphorous Fertilizers

Compound	Process Energy GJ/ton	Cumulative Energy GJ/ton	P_2O_5 Content %	Relative Nutrient Energy GJ/tonP_2O_5
Phosphate Rock	0.86	0.86	33.4	2.57
Phosphoric Acid	0.36	3.00	37.6	7.97

→ Total energy cost: 7.97 GJ/ton P_2O_5

2.3.6   Comparisons

Mudahar and Hignett (1987) have for 1979, 1981 and 1983 compiled a detailed investigation of the energy used in the production of fertilizers, including sulphur and phosphorous. It appears that their work is the basis of many other reports as their figures and assumptions are frequently mentioned. Concerning the assumption of zero energy charge for the recovery of sulphur, when using sulphur-burning sulphuric acid production plants net energy gains are present. Following more or less the same process chain as list in the methodology a selective comparison can be created (see Table 9 & 10).

Table 9   Sulphur Production with Zero Energy Charge

Year	Process Energy GJ/ton	Cumulative Energy GJ/ton	Sulphate Content %	Relative Nutrient Energy GJ/tonSO$_3$
1979	-1.32	-1.32		-0.528
1981	-2.14	-2.14	250	-0.856
1983	-2.18	-2.18		-0.872

→ Total process energy: -0.872 GJ/ton SO$_3$

Table 10   Phosphoric Acid Production Related to Zero Energy Charge for Sulphur

Year	Process Energy GJ/ton	Cumulative Energy GJ/ton	P$_2$O$_5$ Content %	Relative Nutrient Energy GJ/tonP$_2$O$_5$
1979	7.44	3.77		7.25
1981	6.08	0.13	52.0*	0.25
1983	4.86	-1.20		-2.31

- These values are expressed in ton of P$_2$O$_5$ and the average grade, in this case 52%$_{mass}$

→ Total process energy: -2.31 GJ/ton P$_2$O$_5$

The process parameters are not exactly identical to the chosen European BAT of 2000, but are comparable; nonetheless the trend can be clearly seen that by already 1983 phosphorous has a net energy gain due to the zero energy charge of sulphur recovery. The rapid transformation from an energy intensive process chain to a net energy gain is most likely attributed to the energy crisis of 1979 and the increased attention to energy efficiency at the time.

Many life cycle assessments have been conducted investigating the energy requirements of fertilizers and phosphorous being a primary nutrient is always included (see Table 11 & Figure 4).

Table 11   Overview Phosphorous Production Energy

Source Author	Year of Publication	Fertilizer Type End Product	Relative Nutrient Energy GJ/tonP$_2$O$_5$	Comment
Bertianume[19]	2001	All	6.80	Partly based on Pimentel
Biermann[20]	1999	P-acid	15.80	1997, Modern European
Brehmer	**2006**	**P-acid**	**7.97**	**2000 BAT energy charge**
Brehmer	**2006**	**P-acid**	**-5.35**	**2000 BAT zero energy**
Mudahar[2]	1987	All	-2.31	Select 1983 zero energy
Patzek[21]	2004	SingleSuper	6.80	30-year old technology
Pimentel[22]	2001	SingleSuper	17.44	45-year old technology
Shapouri[23]	1995	SingleSuper	4.76	Partly based on Pimentel
Shapouri[24]	2002	P-acid	3.90	Greet model 2000
UFl[25]	1991	All	8.50	Based on Mudahar
Wang[26]	1999	All	11.40	Partly based on Pimentel

As previously mentioned the Frasch process (see Figure 5) is no longer a major contributor to the industry as it used to be, currently representing about 2% of the world total. It involves high process energy in the form of superheated water (160°C) and compressed air. Only the figure selected from Mudahar is negative because the other studies have taken industrial averages for all

the various production processes along the chain from sulphur (including Frasch) to phosphoric acid. There is no apparent reason why, but many of the newest studies continue to use obsolete data. In any case, it is observable that without the zero energy charge even the most state-of-the-art production processes are in the range of some of the most pessimistic and outdated technological averages. For comparison using the zero energy charge assumption with the BAT of 2000 yields an associated production energy of -5.35GJ/ton. That leaves an overestimation difference between 9.3 – 22.79GJ/ton.
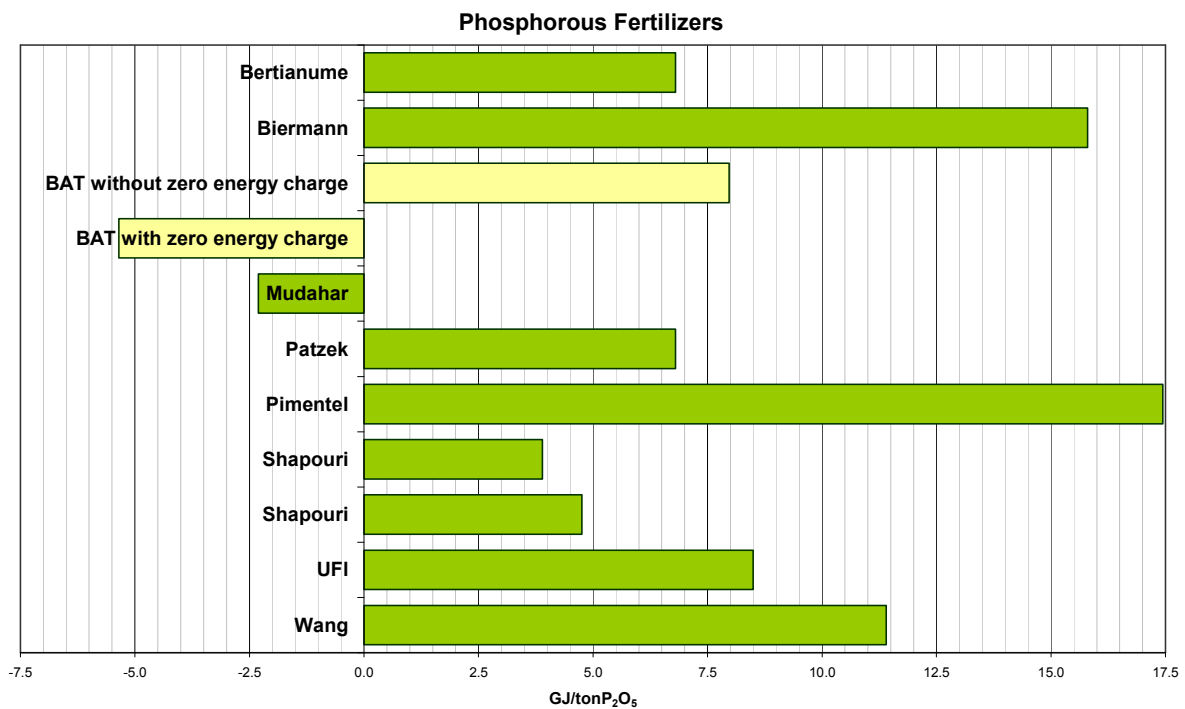
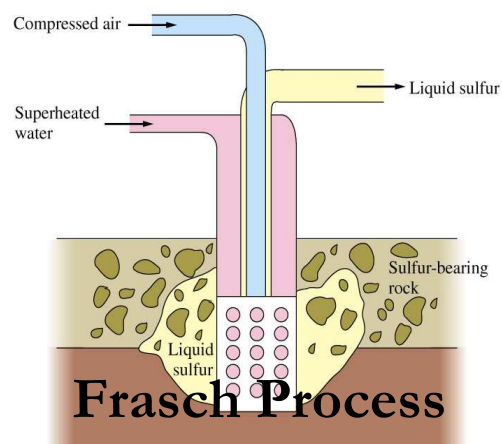Figure 4   Overview Phosphorous Production Energy

Figure 5   Frasch Process

2.3.7 Exergy

As an additional indication factor the same calculations were expanded upon by converting the material and energy streams to the common term exergy. For simplification reasons the minor contributor, mixing exergy potential, has been excluded leaving the physical and chemical proportions for the calculations. By including entropy from the steam charts the same relation between pressure and mass flow are converted to exergy. Cumulative exergy for electricity is 35%. Chemical exergy of the various streams were taken from [21]. The following table (Table 12) illustrates the calculation method applied for the entire chain starting with a sulphur feedstock (H_2S) exergy content of 20.86GJ/ton. H_2S and S have a resulting chemical exergy of 23.83GJ and 17.89GJ/ton, respectively. 20.86GJ/ton is found by the same 50% contribution assumption as with the calorific value. By combining the chains, essentially a cumulative exergy calculation (CExC) is performed, which like for energy, is a far better indicator than the absolute process exergy. (see Table 13 & 14)

Table 12   Exergy Calculation Outline for Sulphur

	Component	Symbol	Quantity	Exergy	
Input	Hydrogen Sulphide	H_2S	1.066ton	20.86GJ/tonH_2S	22.24GJ
	Dry Air	Air	2.162ton	0.124GJ/tonAir	0.268GJ
	Electricity	kWh	0.19GJ	1 (Ex/En)	0.19GJ
Output	Sulphur	S_2	1	19.01GJ/tonS_2	19.01GJ
	Steam (0.8MPa)	H_2O	0.370ton	0.784GJ/tonSteam	0.29GJ
	Steam (4.0MPa)	H_2O	2.23ton	1.003GJ/tonSteam	2.24GJ

- Listed are only the major streams, the minor (trace and waste) streams were also taken in consideration for the final calculations

Exery Input: 22.70GJ/tonS_2

Exergy Output: 21.54GJ/tonS_2

→Total process exergy: 1.16GJ/ton S_2

Table 13   Exergy Overview for Sulphur Chain

Product	Input (GJ/ton)	Output (GJ/ton)
Sulphur	22.70	21.54
Sulphuric Acid	1.06	4.26
Phosphate Rock	0.73	0.06
Phosphoric Acid	1.40	3.08

Table 14   Cumulative Exergy Overview for Sulphur Chain

Compound	Process Exergy GJ/ton	Cumulative Exergy GJ/ton	Nutrient Content % (P_2O_5 or SO_3)	Relative Nutrient Exergy GJ/ton (P_2O_5 or SO_3)
Sulphur	1.16	1.51	250	0.61
Sulphuric Acid	-3.20	3.28	63.6*	5.16
Phosphate Rock	0.67	1.14	33.4	3.41
Phosphoric Acid	-1.68	6.57	37.6	17.48

- Dilution to 78%H_2SO_4

→ Total exergy cost: 5.16 GJ/ton SO_3

→ Total exergy cost: 17.48 GJ/ton P_2O_5

2.3.8   Other Exergetic Studies

The research field of exergy is still a relatively new topic meaning that the amount of studies available is limited. Szargut et al. (1988) have calculated to great detail a sulphuric acid plant based on sulphur burning. Following their calculations the process exergy is 5.273GJ/ton (11.8GJ/ton CExC) relating to 4.72GJ/tonSO$_3$. van der Velde (2003) had used the same base information and applied it to phosphoric acid for use in the fertilizer industry. Following those calculations the process exergy is 8.33GJ/ton (25.6GJ/ton CExC) relating to 35.1GJ/tonP$_2$O$_5$. However both of these sets of exergetic calculations are based on traditional elemental ore mining (Frasch process). That takes into consideration the chemical exergy of the ore and the processing, meaning the figures are of a different nature than those calculated above. Regardless, they do illustrate that the exergy costs of sulphurous and phosphorous fertilizers are significantly higher than energy.

2.4   Results and Discussion

Calculating the process energy of fertilizer products is nothing new, many independent studies and reports have been conducted. Yet, generally speaking such reports are based on industrial averages of outdated technologies. Sulphur is an interesting chemical which illustrates this weak point perfectly as recent governmental legislation and technological developments have rapidly shifted the industry. Desulphurization of transport fuels has in the last 10 years emerged as a major source for sulphur production and it can be expected that, in as little as a matter of years, the desulphurization of fossil fuels will become the primary source of sulphur. As this emerging trend is realized and downstream fertilizer production become ever more energy efficient, the previous assumptions must be re-evaluated. Pertaining in particular, to the reports derived from process technologies of several decades ago and their formally associated production distribution, the zero-energy charge was only a minor factor in the resulting figures. They involve highly energy intensive processes with little apparent energy recovery and efficiency, so in contrast the offset of a free feedstock source was practically negligible. While analysing the current best available technology both phosphoric acid and sulphuric acid have large net energy gains leading to the notion of reassessing the previous assumptions; for it just seems illogical for bulk commodity products that are heavily employed as primary growth stimulators to have a net energy gain.

The intensity of fossil fuel extraction is still on the rise while the quality is on the decline, which will in turn raise sulphur production. Previously petroleum companies were merely producing sulphur as a by-product; they are now a primary producer. The traditional demand for sulphur, the fertilizer industry, is not increasing as quickly as the supply of sulphur from desulphurization processes. It is expected that by 2011 between 5.9 and 12.1Mton of surplus elemental sulphur will be present [4]. This will most likely trigger the price to fall, but burning the access for energy production would be incorrect if assumed as a zero energy charged source. This may not be in the minds of industry at present but with around 10Mton annual surplus it just might. Sulphur is not for free.

Biomass utilization is under constant debate whether it is energetically positive. Fertilizers are one of the primary contributions of (direct and indirect) energy input and having a net energy gain for an input is misleading. For in fact, as the calculations show, both sulphurous and phosphorous fertilizers are not energy positive but energy consuming in the form of a feedstock cost. Using the most recent figures available will make the biobased economy look progressively more attractive, but all issues and previously made assumptions should be carefully readdressed for new technological developments. Sulphurous and phosphorous fertilizers are possibly just one issue which needed to be paid closer attention to. Sadly the issue of charging sulphur with a feedstock cost slightly argues against the energetic benefits of biomass utilization, whereas readdressing other sectors may very well yield more encouraging figures.

An option to circumvent high energy input streams for the biomass agronomy is recycling and closed loop integration. The production of phosphoric acid produces 4.8ton of phosphogypsum for every ton of P_2O_5 equivalent. Phosphogypsum has the formula $CaSO_4$ and can present positive benefits when added to the soil [28]. It can supply the soil with calcium ions (Ca^{2+}) and sulphate ions (SO_4^{-2}) Both can be used for their nutrient properties while not affecting the pH level. Gypsum is also regarded as having soil amendment properties; promoting structure and ion exchange. The only drawback is that traditional pH balance measures supply sufficient level of both nutrients. This example is merely presented as a way of thinking to mitigate high energy related products in the biomass production chain, like the sulphur based fertilizers.

2.5   Conclusion

Energy is never for free; it can only be transformed as stated by the first law of thermodynamics. Applying a feedstock energy cost to the sulphur contained in fossil fuels when subsequently used in sulphuric acid production results in a potential higher heating value of 25.2GJ/ton S. This relates to 2.27GJ/ton SO_3 and 7.97GJ/ton P_2O_5 for the first stage fertilizer products. Each transformation of energy results in a degradation of the work potential of the energy source as stated in the second law of thermodynamics. Processes involving a multitude of process steps are best described in terms of exergy. Applying a feedstock exergy cost to the sulphur contained in fossil fuels results in a potential chemical exergy of 20.9GJ/ton S. This relates to 5.16GJ/ton SO_3 and 17.48GJ/ton P_2O_5 for the first stage fertilizer products. These values represent the current best available technology and expected trends for the near future. Assumptions are essentially simplifications and should be carefully criticized when conducting a life cycle analysis. Regarding sulphur and its resulting products the previous assumptions can no longer hold true for the recent development of the sector. No longer should sulphur be regarded as energy free.

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2

2

Using an energetic and exergetic life cycle analysis to assess the
best applications of legumes within a biobased economy

3

Abstract

In symbiosis with bacteria, legumes are able to biologically fix nitrogen from the atmosphere and therefore require less artificial nitrogen fertilizer. As the manufacturing of nitrogen fertilizers demands a lot of process energy, growing legumes may give large overall energy savings. The reduction of nitrogen fertilizer, however, gives a yield loss as the carbon-to-nitrogen efficiency is lower for inoculation than for the synthetic process. When brought into the realm of biomass for bioenergy, the energy savings obtained through less fertilizer input must be balanced with the loss of potential yield output. Twelve popular choice crops (including two legumes, two crops grown in mixture with legumes and one crop associated with mycorrhiza) were chosen to investigate the relationship between solar radiation input, fertilizer input and the resulting potential bioenergy output. A cradle-to-factory gate assessment was performed with cumulative energy and exergy values as the main indicators. The trade-off between lower fertilizer energy inputs to utilized solar radiation was assessed. Combined they relate to the land use efficiency, basically the energy relations per hectare. Our analysis shows that legumes do not present energy savings and do not contribute to sustainability when grown as bioenergy crops. The benefits of nitrogen fixation by legumes should be carefully assessed and best utilized within the emerging sector of non-food applications.

Keywords

LCA, exergy, energy, land use efficiency, legumes, solar radiation, fertilizers

3.1 Introduction

The Leguminosae family is unique in the plant world as plants from this family are able to form a symbiotic relationship with certain bacteria, mainly *Rhizobium spp.* The bacteria inoculate the root structure and there thrive off of the saccharides flowing in the xylem stream while in exchange providing nitrogenous compounds to the plant, either directly (excess nitrate) or indirectly (after decomposition of dead bacteria or plant material). This remarkable feature enables *legumes* to naturally fix atmospheric nitrogen, dubbed as biological nitrogen fixation (BNF). The ability to form this symbiosis reduces the nitrogen (N) fertilizer application rates in agricultural practices. The potential BNF for most species is in the range of 200 to 300 kgN/ha per year, with a maximum above 450 kgN/ha[1]. Before the advent of synthetic fertilizers, it was common practice to always incorporate a leguminous crop in the rotation to maintain soil fertility. Today, due to the higher productivity of high-external-input farming, only in scarcely populated and/or low-income regions are legumes still common in crop rotations[2]. Artificial N fertilizers are a convenient and cheap source of N[1]. Yet, generally BNF is considered economically advantageous and sustainable[2]. As the associated production costs of N fertilizers are energy intensive, legumes are commonly assumed to yield energy savings[3]. This notion indeed holds true when solely focusing on the cumulative process energy costs of N fertilizer production in relation to the different application rates. However, investigating the entire process chain reveals that this notion is incomplete. When extended into the realm of biomass-for-bioenergy purposes legumes are actually more energetically intensive. The main reason behind this lies within the theoretical and practical axioms of legumes crops: *"Although N_2 fixation represents an economy in terms of the cost of agricultural production, accruing nitrogen in this way is not "free" in terms of plant growth"*[4]. It is the loss of yield and thus captured solar energy that when brought into a proper comparative LCA explains that in fact legumes are more inefficient in terms of energy and land utilization.

3.1.1 Article Purpose

This paper will prove that legumes are not the most logical choice for use in the biobased economy as an energy crop. Nothing is "free" in this world, including solar energy (in terms of land) and fixed N (in terms of yield); there is always a trade-off and this trade-off will be determined. The bottom-line is to reassess the role and potential use of legumes in the biobased economy as the agronomics of food and non-food applications have different criteria.

3.2 Methodology

3.2.1 Goal and Scope

The standard methodology of the ISO14040 series has been followed to a great extent with the exception that only the major material streams, energy and exergy values, were documented and no environmental considerations were made, as only the resulting process energy and exergy are of interest in the analysis. Furthermore, the cradle is set at the input of fossil fuels for the extraction of minerals or chemical synthesis and the grave is set as the potential calorific values of

the crops. Essentially, a limited exergetic cradle-to-factory gate assessment is conducted to determine the entire process energy and exergy for the production of the fertilizers to its use in biomass cultivation along with the captured solar radiation.

Net Energy Value (NEV), or the ratio of input energy versus output energy, is a widely used indicator for the biomass sector. Net Exergy Value (NExV) follows the same principles for exergy terms. As the nature of this work is to argue the near future energy requirements for biomass implementation, the best available technology was chosen for each of the fertilizer production processes. They will presumably be standard practices in the near future, basically representative of when biomass is expected to be heavily implemented.

3.2.2   Data

Several crops are already considered as classical crops for bioenergy and biomaterials. Twelve such common bioenergy crops have been selected for the investigation. Production and climate data for the crops are based on the regions of high production with a high degree of expertise, essentially representing the current best agricultural practices. Listed in Table 1 are the 12 crops, associated regions and typical degree of natural nitrogen fixation for the yields.

Table 1   Choice of Crops Species

Botanical Nomenclature	Common Name	Continent	Country/State	Type	Inoculation Degree
Beta vulgaris	Sugar beet	Europe	Germany	Non-legume	0%
Brassica napus	Rapeseed	Europe	Belgium	Non-legume	0%
Glycine max	Soya bean	North America	Illinois	Legume	100%
Helianthus annuus	Sunflower	Europe	France	Non-legume	0%
Medicago sativa	Lucerne	North America	South Dakota	Legume	80%*
Lolium perenne	Perennial ryegrass	Europe	Netherlands	Non-legume mixed with legume	59%†
Panicum virgatum	Switchgrass	North America	Iowa	Non-legume in symbiosis with AMF	30%**
Saccharum officinarum	Sugar cane	South America	Brazil	Non-legume mixed with legume	70%‡
Solanum tuberosum	Potato	Europe	Netherlands	Non-legume	0%
Sorghum bicolor	Sorghum	Africa	Kenya	Non-legume	0%
Triticum aestivum	Wheat	Europe	France	Non-legume	0%
Zea mays	Maize	North America	Iowa	Non-legume	0%

*To obtain the high yield additional fertilizer must be added, 80% is typically covered by BNF[5]
**Arbuscalar Mycorrhizal Fungi (AMF) present in poor soils of Midwest, promote nitrogen and phosphorous uptake, covers around 30%[6, 7]
†White clover is mixed at typically ratio of 37% to cover 59.4% of the nitrogen demand, but varies throughout the cultivation period[5, 8]
‡Common practice in Brazil to mix green leguminous manure, covers 70% of nitrogen demand[5, 9]

3.2.3   Impact Assessment

Both energy and exergy are chosen as the impact categories to evaluate the costs along the process chain. Exergy, the quality of energy or maximum obtainable work, is mainly included to provide further depth in the energy efficiency of the processes particularly those involving large temperature differences. Yield figures will be expressed in terms of total (fruits, tubers, stem, leaves, etc.) dry weight per area (ton/ha) and will be used to calculate the energy/exergy output in

terms of GJ/ha. As both the solar radiation and fertilizer process requirements will be related to the land input, the resulting term will also be in GJ/ha. Leaving the final indication term which expresses the inputs and outputs as a percentage for graphical and tabular comparison, the so-called *"net energy value"* and *"net exergy value"*.

3.3 Calculations

3.3.1 Crop Output

3.3.1.1 Yields

Presentation of biomass yields figures vary heavily depending on the crop; listed from the wet weight of the harvestable component (like with tubers) to the total dry stover (like with fodders). In conforming to standardization all figures must be converted into one common term: total dry biomass. This is the total *above ground accumulation* with the clear exception of tuber-based crops. Rooting system can constitute a considerable quantity of mass structure, for example, the rooting system of winter wheat can reach depths of up to 2 m and represent around 10% of the total dry biomass. Legumes in particular have a dense sub-soil biomass material accumulation due to bacterial inoculation. But, due to the overwhelmingly high expenses linked with harvesting and isolating root mass plus the added soil benefits of leaving the rooting systems in place (e.g. protection against erosion, maintenance of soil organic matter), this biomass portion will be excluded. Overall dry weight figures are determined by using the known yields data figures, weight proportions and moisture content of the different plant components.

> For example: Soya bean has a listed yield of 2.61ton/ha harvestable seeds as a 3-year average in the Illinois region. It is known that seeds contain 10.2% moisture, comprise about 1/3 of the total dry weight and that the stover has a moisture content of 60%. This results in a total dry weight yield of 7.1ton/ha and a total fresh weight yield of 14.5ton/ha.

Figure 1 illustrates the resulting total wet and dry weight of the 12 selected crops

3.3.1.2 Composition

Biomass is best broken down into seven basic categories: simple carbohydrates (like sugars and starch), complex C6 carbohydrates (like cellulose), complex C5 carbohydrates (like hemicellulose) lignin, protein (including free amino acids), fatty acids (or oils) and minerals (when combusted referred to as ash). The composition of each plant component for each crop is well documented and, by following the same procedure as with the yield calculations, can be brought to represent the total crop. Figure 2 illustrates the resulting proportions for each crop.

3.3.1.3 Calorific Values

The biochemical constituents can be assigned enthalpy and exergy formation values by implementing the group contribution method. Table 2 presents the overview of the individual biochemicals following the group contribution method. Figure 3 illustrates the difference in

energetic and exergetic output potential per land area by incorporating the yield, composition proportions and the formation values together
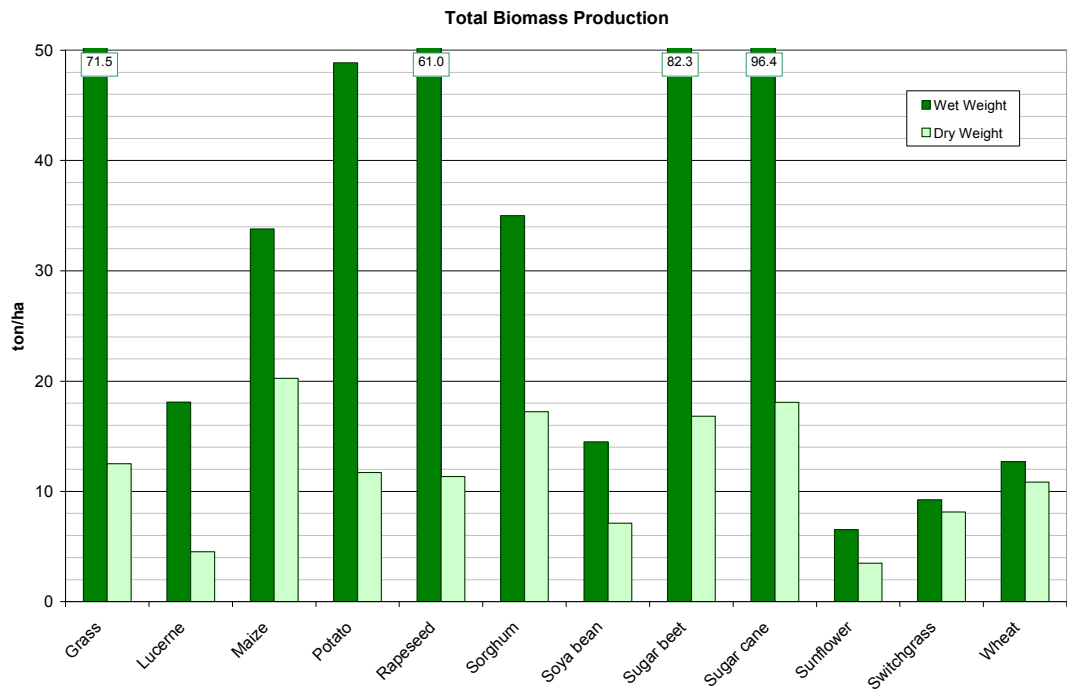
Total Biomass Production

Figure 1   Crop Wet Weight and Dry Weight Yields
- Yield Data: 5-year average (2001 – 2005) from FAOSTAT[10]
- USA based crops use a state-based 3-year average (2002 – 2004) from USDA[11]
- Grass[5], Lucerne[12] and Switchgrass[6] being strictly non-food crops are based on regional listed averaged practices.
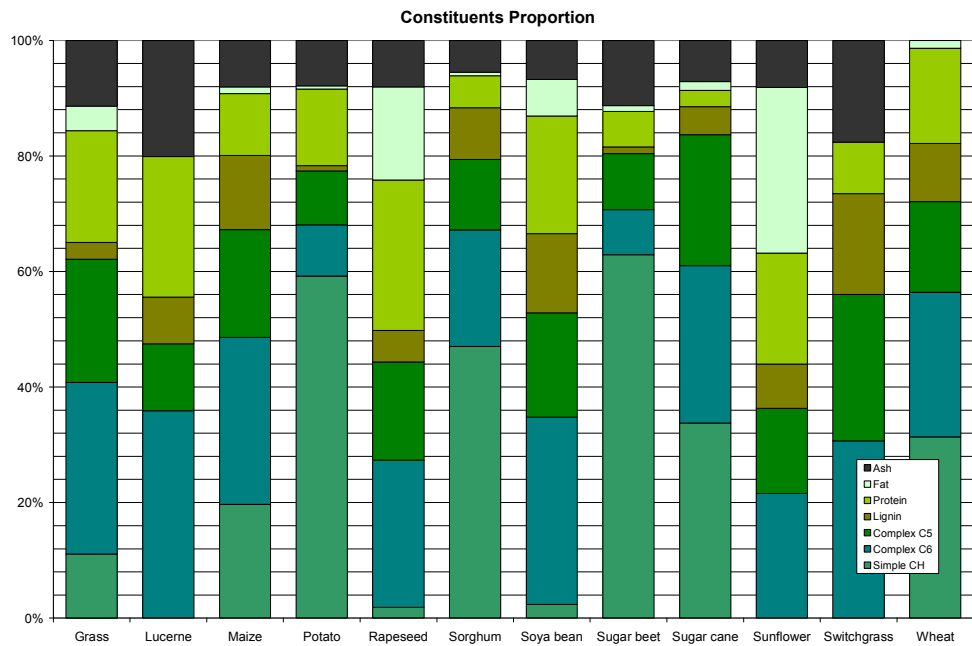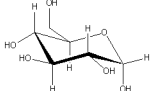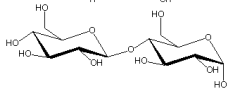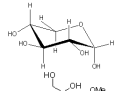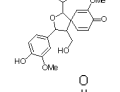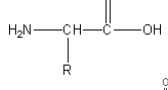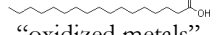
Constituents Proportion

Figure 2   Crop Biochemical Constituents Proportions
- Crop composition: (mainly) Duke Handbook of Energy crops[12]

Table 2   Group Contribution Calorific Values (MJ/kg)

Constituent	Representative component	Structure	Enthalpy	Exergy
Simple Carbohydrates	Glucose		13.79	16.70
Complex C6 Carbohydrates	Cellobiose		14.63	17.64
Complex C5 Carbohydrates	Xylose		13.07	16.05
Lignin	Lignin section*		25.56	27.59
Protein	Amino Acid†		18.43	22.61
Fatty Acid	C17		40.23	43.09
Ash	Mix‡	"oxidized metals"	2.43	2.89

- Chemical group contribution: formation enthalpy and exergy from Szargut[13]
*common reoccurring section in the lignin structure
†protein consists of 20 different amino acids, this is the so-called "base" or representative amino acid, the "R" is CH_3
‡common mix is 35% SiO_2, 30% K_2O, 15% CaO, 10% P_2O_5, 5% TonO and 5% Na_2O
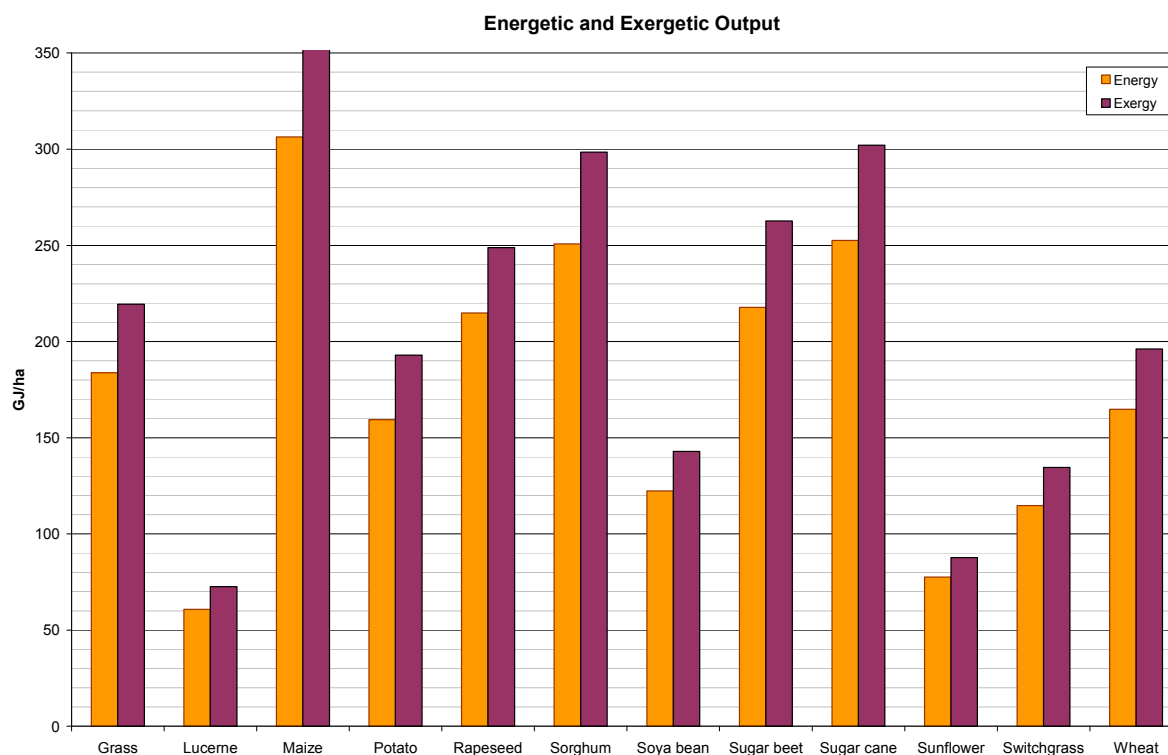

Figure 3   Crop Energetic/Exergetic Output

3.3.2   *Solar Radiation Input*

3.3.2.1   Location

The level of incoming solar radiation is different for all the crops as it is highly dependent upon the relevant regions of growth. Incoming solar radiation is expressed in terms of kWh/m^{-2} for each month and can be easily converted into MJ/ha. Solar radiation has a conversion factor of 0.9327 for energy to exergy[14].

3.3.2.2   Growth Cycle

What is important to consider when determining the incoming solar radiation is the amount actually used by the crop. Effectively when the crop or seedlings are physically occupying land space, for in some cases the land is not occupied year-round and during such periods the solar radiation is not used by the crop. And in theory a cover crop could be cultivated yielding additional biomass and thus utilize a greater portion of the regional solar radiation. By using the common agricultural practices in the selected regions for the particular crops the occupying growth periods are set on a monthly basis. As it is common knowledge it would be superfluous to additionally tabulate these values while Figure 4 visualises the total captured solar radiation for each crop.
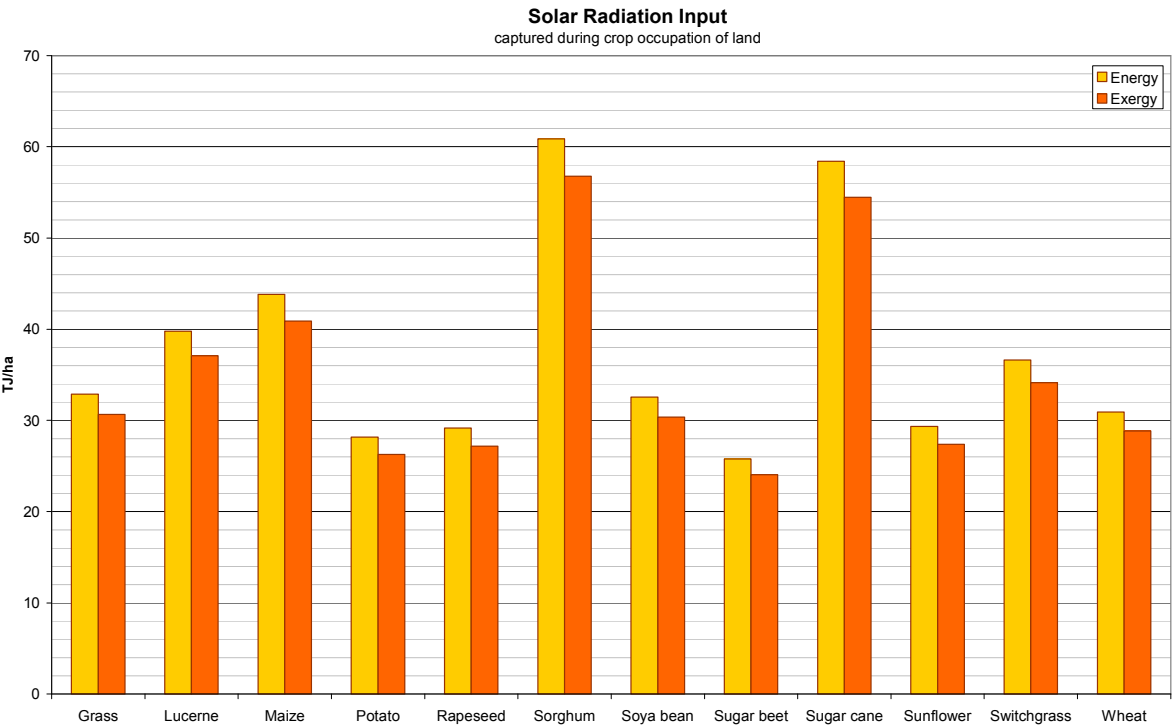

Figure 4   Solar Radiation Input
- Solar radiation: 10-year average NASA Surface meteorology and Solar Energy: SolarSizer Data[15]

3.3.3   Fertilizer Input

3.3.3.1   Process Choice

Aside from CO_2 and H_2O the growth of plant matter is promoted by 12 major nutrients, six of which are taken up in high quantities (kg/ha) and are referred to as macronutrients. Only these macronutrients will be considered and are expressed and calculated to the form common in the industry, namely: nitrogen (N), phosphorous (P_2O_5), potassium (K_2O), sulphur (SO_3), calcium (CaO) and magnesium (MgO). Several assumptions and considerations were made to calculate the most recent cumulative process energy and exergy of the macronutrients. Extensive description and calculations are found in a section of the authors' doctoral dissertation, which is only expected to be published in 2008[16]. In the thesis all of the life cycle inventory (LCI) databases values were rigorously evaluated; here a synopsis of the main points is necessary to highlight the process choices:

- The highest energy efficient processes within the EU from the best available technology of 1999 were chosen[17-25];
- When little or no EU production is available then the highest energy efficient processes within the largest area of world production were taken instead;
- NPK and CAN are the main artificial fertilizer of interest;
- Complete material and energy integration are foreseen;
- Refer to Figure 5 for the process scheme.

Some of the notable considerations made within the individual processes are:

- Sulphur has been assigned a feedstock cost of 25.2GJ/ton energy and 20.9GJ/ton exergy as desulphurization of fossil fuels is not a "free source"[26]
- Phosphate rock processing is based on Florida practices[27]
- Potash mines are based on Saskatchewan practices[28]
- When 1 Ton of NPK is produced 1.6 Ton of CAN is produced

The most common straight fertilizer production route for each of the nutrients has also been included. Table 3 lists the resulting cumulative process energy and exergy demand (CED & CExD) for the fertilizer and process routes in question.

3.3.3.2   Nutrient Uptake

Many chemical analyses have been conducted to document the composition of each crop under a particular yield condition. Such studies determine the proportion of each of the nutrients found in the plant expressed as kg/ton. As the original source data presentation varies the figures have all been converted (using the yield figures) and again conforming to standardization presented in the common term kg/(tonDW). This study results in expressing the nutrient uptake of the crops and is illustrated in Figure 6, essentially providing information for the absolute minimum requirements of the respective fertilizers. As the efficiency of fertilizer uptake versus application rate is dependent on a large multitude of factors like soil conditions, rainfall, fertilizer type and timing of application the factor will be omitted. Over-fertilization is very common under current

practices and results in additional losses and unnecessary soil storage of nutrients. Typically the uptake/application efficiency can range from anywhere from 35%−95%[29] and is generally on the rise with better practices and fertilizer types (like NPK)[25]. In several regions the existing soil fertility is high enough (possibly due to previous over-fertilization) to actual see lower fertilizer application then what is taken up. In such cases the soil is being mined and will eventually require further fertilization. In any case the uptake values presented here are generally an underestimation compared to current application rates, but should come closer to foreseeable scenarios for near future advancements when biomass is likely to reach full-scale implementation.
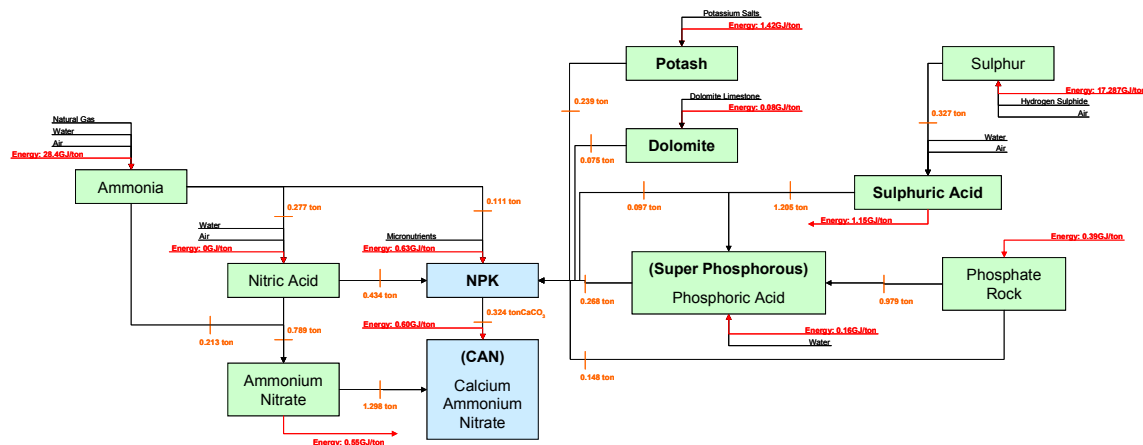

Figure 5   NPK+CAN Fertilizer Simplified Mass/Energy Balance Flow Diagram

Table 3   Fertilizer Production Energy/Exergy

Nutrient element	Nutrient form	Production route	CED	CExD
			MJ/kg	
Nitrogen	Complex (Mix)	NPK+CAN	50.90	53.99
	Straight	UAN	49.02	50.22
Phosphorous	Complex (Mix)	NPK+CAN	25.06	31.63
	Straight	SuperP	7.97	17.48
Potassium	Complex (Mix)	NPK+CAN	5.10	6.31
	Straight	Potash	3.22	4.11
Sulphur	Complex (Mix)	NPK+CAN	2.27	5.16
	Straight	H_2SO_4	2.27	5.16
Calcium	Complex (Mix)	NPK+CAN	0.94	0.74
	Straight	Dolomite	0.16	0.34
Magnesium	Complex (Mix)	NPK+CAN	0.19	0.40
	Straight	Dolomite	0.19	0.40

- Fertilizer Production: EMFA process data for each production step is following the best available technologies[17-25]
- A simplified material process flow diagram of the process is considered (see Figure 1).
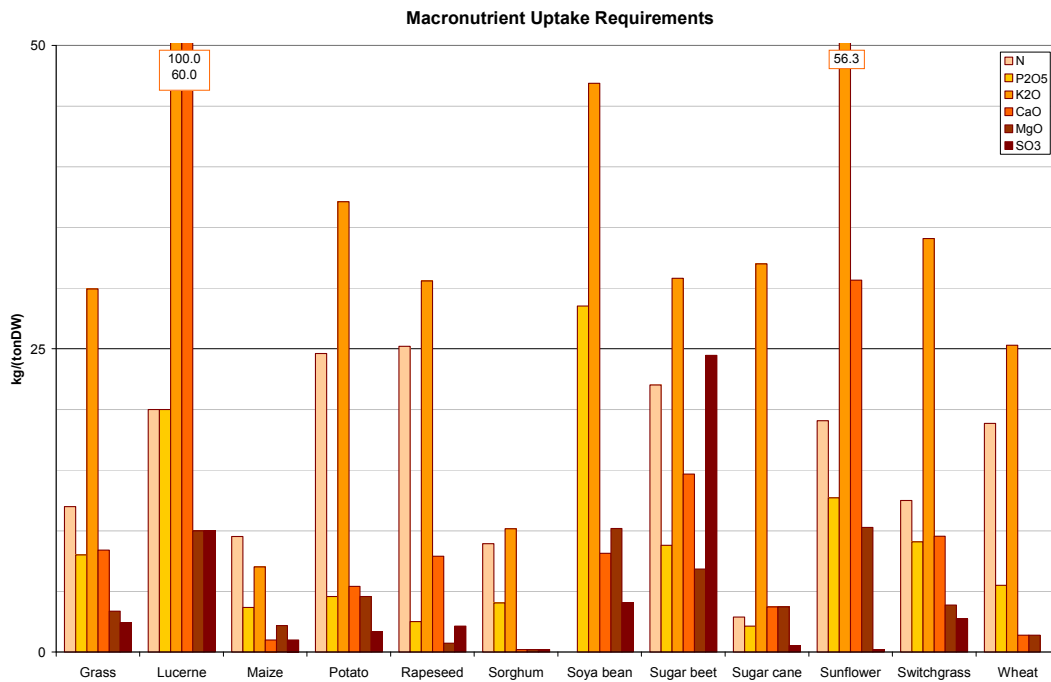- Other specific data will be mentioned upon occurrence.

Macronutrient Uptake Requirements

Figure 6   Nutrient Uptake
- Nutrient uptake: IFA based on the higher or corresponding yield values[5]

3.3.3.3   Energy Relation

By combining both the nutrient uptake level with the nutrient production requirements the total energetic input for the fertilizers can be determined. NPK and CAN cover the brunt of the energy input flows, but due to restrictions in the NPK composition and individual nutrient demands some parameters must be set:

- When any of the macronutrients is larger than 25% of the nitrogen level then that nutrients respective straight route will be used for the dividend;
- When the level of nitrogen is larger than both potassium and phosphorous combined then UAN will be used as the dividend.

The total nutrient energy requirement is displayed in Figure 7.

3.4   Results

3.4.1   Energy Saving or Loss

Table 4 lists the resulting net energy and exergy values (NEV and NExV) for the solar radiation input and fertilizer input components of all the crops. The legumes have a relatively low solar efficiency while indeed having the expected higher fertilizer efficiency. The average solar radiation NExV is 0.58 for all the listed crops, 0.70 for non-legumes and for legumes it is 0.43. That represents a solar radiation utilization drop of 38.6% for the legumes. The average fertilizer NExV is 1631 for all the listed crops, 1479 for non-legumes and for legumes it is 1935. That represents an increase in fertilizer utilization of 30.8% for the legumes. These figures give a general impression of the trend but do not really stress the point of why legumes are not

advisable as energy crops. The best is to compare some similar non-legumes with legumes to see what the energy savings or losses actually are. Listed in Table 5 is the comparison of 4 different sets of crops. As the solar radiation dictates the potential yield the 2nd crops values have been adjusted using a linear function to match the same solar radiation input. In the scope of potential bioenergy, legumes cost (and not save) an additional 83 – 133GJ/ha in energy and 102 – 181GJ/ha in exergy terms. Should the biomass be combusted in a conventional furnace with a typical electric conversion efficiency of 33%, the overall losses are reduced to 11.3 – 44.2GJ/ha in energy and 15.5 – 67.5GJ/ha in exergy terms.

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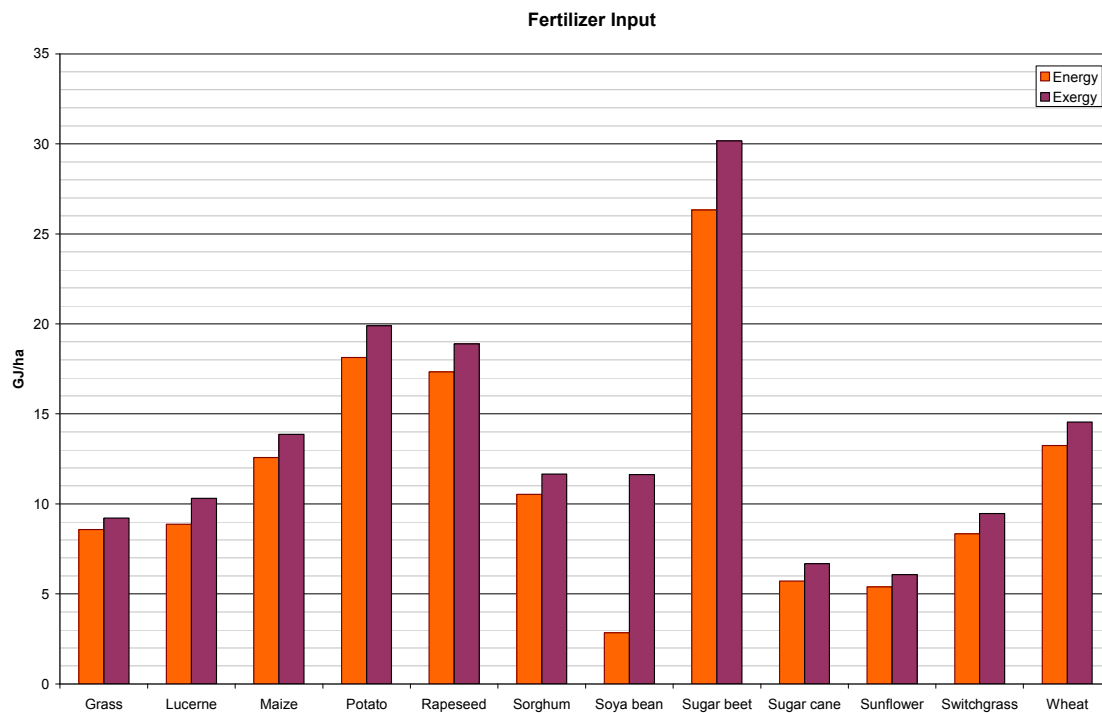
Figure 7   Energy and Exergy of Fertilizer Input

Table 4   Net Energy and Exergy Values

Crop	NEV Solar	NExV Solar	NEV Fertilizer	NExV Fertilizer
Grass	0.56	0.72	2142	2382
Lucerne	0.15	0.20	685	705
Maize	0.70	0.89	2436	2607
Potato	0.57	0.73	879	970
Rapeseed	0.74	0.91	1240	1317
Sorghum	0.41	0.53	2381	2559
Soya bean	0.38	0.47	4292	1229
Sugar beet	0.84	1.09	827	871
Sugar cane	0.34	0.43	3438	3517
Sunflower	0.26	0.32	1439	1443
Switchgrass	0.28	0.35	1237	1280
Wheat	0.31	0.40	726	786

- values are dimensionless, but can be regarded as percentages

Table 5   Legumes versus non-Legumes

| Crop pair | Solar radiation input | | Yield | Calorific output | | Fertilizer input | | Loss | |
	Energy	Exergy	ton/ha	Energy	Exergy	Energy	Exergy	Energy	Exergy
Corn	43.8	40.9	20.2	306	362	12.6	13.9		
Soya bean	32.6	30.4	7.1	122	143	2.85	18.9	133	181
Soya bean (1.35)	43.8	40.9	9.6	165	192	3.84	25.4		
Rapeseed	29.2	27.2	11.4	215	249	17.3	18.9		
Soya bean	32.6	30.4	7.1	122	143	2.85	18.9	90.4	119
Soya bean (0.90)	29.2	27.2	6.4	110	128	2.55	16.9		
Grass	32.9	30.7	12.5	184	219	8.58	9.21		
Lucerne	39.8	37.1	4.5	60.8	72.6	8.87	10.3	132	159
Lucerne (0.83)	32.9	30.7	3.7	50.2	60.0	7.33	8.52		
Sugar beet	25.8	24.0	16.8	209	218	26.3	30.2		
Sugar cane	58.4	54.5	18.1	241	253	5.71	6.68	82.5	102
Sugar cane (0.44)	25.8	24.0	8.0	106	111	2.52	2.95		

- solar input figures in TJ/ha, output figures and loss (non-legume over legume species) in GJ/ha

3.4.2   *Carbon and Nitrogen Efficiency*

Bacteria living in symbiosis with a legume thrive from the carbohydrate source provided by the host plant. It is theoretically proven and logical that the gain in nitrogen comes at the cost of carbon. Atkins has investigated the cost of nitrogen uptake in terms of carbon for the *Lupinus albus* plant[4]. Following the theory the inoculated species requires 2.9 – 6.1gC/gN while when supplied by artificial fertilizer requires 0.8 – 2.4gC/gN. That relates to an extra 2.9gC/gN (using the median) for the inoculation variant. A similar study was performed using experimental fieldwork, taken over a 10-day period during the mid-vegetative period. It concluded that the photosynthesis rate was 2.5gC/plant versus 2.7gC/plant in the nodulated and non-nodulated strains, respectively. This relates to a carbon yield loss of 8% for the nodulated legume. Carbon yield does not reflect the actual yield losses or even the energy losses, but it does comply with the theory that legumes will innately yield less above ground accumulation of biomass.

> Consider: The carbon cost of manufacturing ammonia is 0.695gC/gN whereas the extra carbon demand to biologically fix nitrogen is 2.9gC/gN it would appear obvious that the synthetic route is much more energetically efficient.

Another study in the field of legume carbon and nitrogen economy revealed a 21.1% growth rate increase for non-nodulated legumes[30]. "*Nitrate fed lupins, reducing NO₃ almost entirely in their roots, effected a conversion of 69% of the C of their net photosynthate into dry matter compared with only 56 to 58% in nodulated plants.*"

> Consider: White lupine (*Lupinus albus*) has an average yield of 10.3ton/ha dry weight in its native Australia. A 21.1% yield increase would present 2.17ton/ha extra biomass. Following the group contribution calculations as with the other crops, white lupine has a calorific value of 19.4GJ/ton. This results in 42.1GJ/ha extra bioenergy. The energy saved from mitigating the nitrogenous fertilizer is moderate at 13.2GJ/ha (at 270kgN/ha for 10.3ton/ha) but still relates to an energy loss of 28.9GJ/ha for BNF over artificial nitrogen. The loss is reduced to 9.6GJ/ha following conventional bioenergy production systems.

3.4.3 Dutch Fodder Comparison

Legumes are still heavily employed as fodder material due to their high content and concentration of protein. In the Netherlands it is common to sow a mixture of perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.). A systematic study has been conducted monitoring the effects of nitrogen between ryegrass and clover and under various mixture ratios[8]. Even for this contemporary practice further investigation can raise questions. Table 6 presents a calculation overview for comparing ryegrass with clover under equal Dutch conditions. It reveals that a potential energy loss of 30GJ/ha and an exergy loss of 28GJ/ha is present when using white clover over grass. More importantly are the results from the mixtures, a gain of 6GJ/ha and 20GJ/ha potential energy and exergy, respectively, is present when applying artificial fertilizer. Similar figures are found when incorporating the bioenergy conversion efficiency, although for the mixture an energy loss of -4GJ/ha have been determined. Exergy figures, however, present no such loss. Even the protein yields are nearly identical for all situations; around 2.2ton/ha. Only when focusing solely on fertilizer inputs in relation to protein yields does the leguminous behave outperform; BNF conditions require around 0.6GJ/ton protein compared to 4.5 – 6.4GJ/ton.

Table 6   Dutch Fodder Comparison*

Category	Unit	Ryegrass	Clover	Mix with N	Mix no N
Yield	tonDW/ha	12.2	9.7	11.6	12.8
Clover content	%	0	100	47	21
Calorific value (Energy/Exergy)	GJ/ton	14.6/19.8	14.1/20.9	14.3/20.3	14.2/20.8
Potential yield (Energy/Exergy)	GJ/ha	178/242	136/201	166/236	181/265
Bioenergy yield (Energy/Exergy)†	GJ/ha	59/81	45/67	55/78	60/88
Initial fertilization	kgN/ha	25	25	25	25
Artificial nitrogen demand	kgN/tonDW	19.3	0	0	12.9
Nitrogen cost (Energy/Exergy)	GJ/tonN	50.9/54.0	50.9/54.0	50.9/54.0	50.9/54.0
Nitrogen input (Energy/Exergy)	GJ/ha	13.3/14.1	1.3/1.4	1.3/1.4	9.7/10.2
Total potential yield (Energy/Exergy)	GJ/ha	165/228	135/200	165/234	171/254
Total bioenergy yield (Energy/Exergy)	GJ/ha	46/67	44/66	54/77	50/78
Protein yield	tonDW/ha	2.2	2.1	2.2	2.1
Fertilizer (Energy/Exergy) per unit protein	GJ/ton	6.1/6.4	0.6/0.6	0.6/0.6	4.5/4.8

*Based on WUR field experiments and studies[8]
†Conventional biomass-to-bioenergy combustion furnaces are 33% efficient

3.5   Discussion

The only one attribute making legumes an interesting crop family to consider is the ability to naturally fix nitrogen from the atmosphere. Judging the economic benefit is as simple as checking the fertilizer balance sheet. Following this investigation of 12 selected crops at various inoculation rates reveals that indeed the artificial nitrogen demand is significantly less for crops of a leguminous order, 7.0kg/tonDW compared to 18.3kg/tonDW on average for non-legumes. And under full inoculation conditions the value is of course 0kg/tonDW. Yet, when addressing biomass for bioenergy propagation additional considerations must be made. The harvest material is to be potentially utilized as an energetic source, so the net energy value is all determining. It would appear as a general consensus in the realm of biomass and bioenergy that even today

legumes can contribute to higher energy savings and thus be more sustainable. At first glance it does appear true that savings occur, if the CExD of fertilizer is the only input factor, as the NExV is on average 34.7% lower for legumes over non-legumes. Such a result may conform to the general notion, but under closer examination presents the need for another parameter. When including the yielded calorific values the opposite appears true when comparing crops of a similar nature. As a perfect example, it is suggested that soya bean is a better fodder feed source over corn (maize) as it is more energy efficient[3]. By comparing the two crops under equal conditions presents a contradiction, in fact a potential exergy loss of 181GJ/ha is present for soya bean. That is equivalent to about 3 ton of nitrogen fertilizer. Although the extreme, a similar situation is true for all of other compared crops, with even a loss of 20.0GJ/ha exergy present for grass/clover mixtures under optimal Dutch conditions when relying on BNF. The trade-off between yield-to-energy potential and BNF-to-fertilizer energy savings is not necessary positive.

This result however only covers half the story, namely the relationship of output versus the cumulative fertilizer input. Including solar radiation exacerbates the disadvantage of using legumes for bioenergy purposes. The NExV is on average 38.6% lower for BNF over synthetic nitrogen sources. This means that on average well above a third more land area is required to produce the same amount of potential bioenergy. Biomass cultivation achieves its underlining sustainability from encapsulating the free and abundant source of solar radiation. *"Free and abundant"* is only relative as arable land comes at a cost and is limited. Considering the sheer extent of biomass cultivation needed to meet just a fraction of fossil fuel replacement, land will become a limiting factor. Cultivating a bioenergy crop that would require more land (at no apparent benefit) is a squander of potential solar radiation input. Solar radiation is several magnitudes higher in terms of exergy than the fertilizer input, so seen from this perspective it is a waste of space to plant legumes strictly for energy purposes.

On the flipside, land use is only an issue in regions with expensive and scarce land. In regions where land is cheap and vast the legumes are a good option to keep the price and fossil energy demand down. Only by removing the land factor do leguminous crops seem attractive (i.e. when performance is expressed in GJ/ton and not in GJ/ha). It should however be noted that such regions are generally low in agricultural intensity for a reason, namely low fertility, low natural water supply or low arability. To increase the fertility of depleted regions will take vast amounts of artificial fertilizers where nitrogen is merely one aspect of the macronutrients. Typically legumes require 2 − 3 times more potassium, meaning the problem of one macronutrient may be shifted to another. It is not a coincidence that currently the impoverished regions are the major exploiters of legumes. The advantage of using artificial fertilizers is clear and should be central for biomass production.

All of these points paint a dark picture for the role of legumes in the biobased economy but there are some applications where they can still play a vital positive role. The strong potential use of

legumes lies in their cover-crop potentials. Used as a cover-crop fast growing legumes can provide either additional biomass yields or add to the organic content of the soil. They can also be planted in between harvests to provide a low-intensive form of added soil fertility. Land utilization is not an issue because they will be used to re-supply nutrients and organic matter at times when it is characteristic to leave the field bare. Pasture type legumes crops are best suited as they are capable of establishment and growth during months of either low solar radiation or temperatures.

In addition to bioenergy and biofuels purposes biomass is considered a fitting feedstock for the chemical industry. The calorific value is of no significance when used for chemical production. What is of significance is the so-called fossil fuel mitigation potential, including feedstock and process energy aspects. Fermenting carbohydrates will produce a high quantity of chemicals that contribute to reducing the naphtha feedstock. Hypotheses have been discussed and laid out for the additional utilization of proteins in biomass as precursors for the bulk chemical industry[31]. These functionalized chemicals have a much larger fossil fuel mitigation potential than typical biochemicals, biofuels and bioenergy. Legumes, in absolute terms, do not produce more proteins or fatty acids than non-legume per land area. They are however present in higher concentrations, well above the 10% common in leafy material. The benefit of higher concentrations is reflected in the bioprocessing intensity which is conceivably a fraction of the cost. Much work still needs to be investigated in properly determining the extent of the functionalized chemical production potential. So, the industry will be posed with the task to determine the economical trade-off between fertilizer reduction, increased land requirements and chemical production.

3.6 Conclusion

The biobased economy relies on the notion of providing as much energy savings as possible at the lowest energetic input as possible; essentially striving for the highest net energy value to replace fossil fuel dependence. It seems only natural to assume that because little or no nitrogen fertilizer is added to legume cultivations that the energy efficiency is higher. The fact that the yields are lower are disregarded or underestimated as bearing no particular consequence. What must be taken into consideration is the potential exergetic output lost caused by those lower yields. Only by relating the reduction in fertilizer exergy input to potential exergy output loss can such an assumption be validated. By performing such an investigation for several choice crops it is apparent that the hypothesis must be repelled. In the extreme cases, exergy losses in the vicinity of 100GJ/ha occurs when relying on biological nitrogen fixation. A lower yield also has the obvious negative effect on land use efficiency. Bringing the exergetic solar radiation utilization into account reveals that legumes necessitate roughly one and a half the land space for the same bioenergy potential. As biomass cultivation will require vast land areas to provide the necessary feedstocks to the industry cost minimization and maximum land utilization is fundamental to the success. Legumes will have their benefit when land is not an issue, but as the arguments continue over the high biomass land demand low solar radiation usage is not acceptable. Legumes are not suited for bioenergy production and as opposed to popular notion are not more efficient. The

biobased economy is not limited to bioenergy propagation and each biomass feedstock type must be assessed for the best application as no one crop is best suited for all aspects. Within the bioenergy sector legumes will remain attractive only when viewed as cover-crop candidates.

3

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Assessing the current Brazilian sugar cane industry and directing
developments for maximum fossil fuel mitigation for the
international petrochemical market

4

Abstract

The EU proposes that 5.75% of the transportation fuels market consist of biofuels by 2010 and the US propose that all gasoline be blended with 10% bioethanol by 2012. While these targets have not yet been reached an aura of critique is emerging, arguing that biofuel mandates are not sustainable. One of the major ensuing topics surrounding biofuel sustainability is the food versus fuel debate in reference to 1st generation (or food-based) technology. This article will reveal that for the specific case of sugar cane in Brazil, 1st generation bioethanol is more sustainable than expansion to include 2nd generation (non-food based) technology. Two life cycle assessments are conducted, firstly a cradle-to-factory gate analysis with focus on fossil fuel reduction potential. Fertile land is consumed and occupied by all biomass crops, the biomass option with the highest mitigation potential per land can be considered the most sustainable and least intrusive to food production. Ethanol on average can mitigate 104GJ/ha/a, which is equivalent to 17barrels of oil annually. This can increase to 353GJ/ha/a for the foreseeable best practice situations, higher than the 2nd generation option. A first step biorefinery producing ethylene achieves 509GJ/ha/a. Secondly, the BASF developed eco-efficiency model, which links both environmental impacts and economic profitability into one easy to interpret graph, is used as validation. Overall it is calculated that a best practice 1st generation ethanol and its later dehydration to ethylene are the most eco-efficient options. The biobased economy deserves highly specific assessments.

Keywords

LCA, Eco-Efficiency, Ethanol, Ethylene, Sugar Cane, Brazil, Energy

4.1 Introduction

In recent years, the interest and attention surrounding biofuels has quickly catapulted to the forefront of the impending fossil fuel debate. Politicians in both the US and EU have been swift at calling for fuel blend mandates: the EU proposes 5.75% (energy content) of all transportation fuels to contain biofuels by 2010 while the US proposes 10% (E10) to be the minimum grade for gasoline by 2012[1, 2]. Biofuels are generally understood as any fuel originating from biomass that behave similarly and can be employed to displace existing liquid transportation fuels within internal combustion engines (gasoline, diesel, etc.). The two major types of particular interest are bioethanol for gasoline and biodiesel for diesel. Conventional technology or 1st generation biofuels are based on converting the edible portion (starch, sugar, oils, etc.) of food-based crops. Newly researched and developing conversion techniques are capable of converting the residual portions and non-food-based crops, called advanced biofuels or 2nd generation. As the biofuels sector expands and evolves into a separate industry an aura of critique is emerging arguing that the US, EU and other developed nations biofuel mandates are not sustainable[3].

The major focus is on the 1st generation production methods with the title of the most recent OECD report iterating the standpoint *"is the cure worse than the disease"*. Ecologically driven NGO's (like Greenpeace and the WWF) further support this notion by calling attention to the moral consequences of biofuel utilization such as food shortages to the destruction of natural habitats while pointing out the minor impact on climate change solutions. They universally claim that *most* biofuels from the 1st generation are not as efficient as simply using petrol or diesel directly[4]. The general sentiment is that it is best to wait until 2nd generation biofuels have reached maturity. For example, a science article stated *"Ethanol produced from cellulosic material (switchgrass) reduces both GHG's and petroleum inputs substantially"* in respect to standard 1st generation options[5].

The problem is one of generalization; *"most"* biofuels is uttered but the stance could very well hold for *"all"* biofuels. According to the OECD report, only 21% of respondents believe in the potential of 1st generation biofuels (made from agricultural crops) to *"lower overall carbon levels in the atmosphere without unacceptable side effects"*. This year on April 4th, the German Environmental Minister announced that the country will not raise the compulsory bioethanol blending figures beyond 5% while adding *"with imports there is no guarantee that it is produced using sustainable production methods"*[6]. The EU deliberated not a week later discussing a possible suspension to the expansion plans of their biofuel mandates, now regarding them as being *"overambitious"*[7]. Studies systematically reveal that for bioethanol, 2nd generation technology are most sustainable. This may very well hold true for US-based crops and EU-based crops but is definitely not the case for all crops in all regions of the world. Assessment of biomass production chains must be performed for each crop in each region without the tendency to generalize[8]. This article will reveal that for the case of sugar cane in Brazil, 1st generation bioethanol is more sustainable than the expansion to include 2nd generation.

Countless numbers of studies both internally and externally have been conducted with regards to the Brazilian sugar cane-to-ethanol industry. It has consistently been a focal point since their National Alcohol Program (Pró-Álcool) commenced and of last proofed successful. Many older studies, however, provide poor data sets which contradict with one another and were frequently published exclusively in Portuguese. UNICA, the São Paulo Sugar Cane Agroindustry Union, recently published a detailed book (in both Portuguese and English) compiling twelve individual studies into a one clear and legible format[9]. It has since been widely acknowledged that this region with this crop provides a highly positive fossil fuel savings, in the order of 8 (or 8 units of energy out for every unit invested)[10].

A *net energy value* (NEV) of 8 is considered the norm and a value to strive for in other regions. Other cropping systems, namely US-corn and EU-wheat, struggle to obtain values beyond 2[11, 12]. Yet, the impressive NEV of 8 is overlooked because in regards to sustainable production further expansion of sugar cane plantations is frequently blamed for contributing to Amazon deforestation. The real problem lies in illegal deforestation and lack of property rights and the local opinion on the matter is that it is a coy act of protectionism of the "Northern" countries to develop their own 2nd generation (or equivalent) technologies[13, 14]. While the current ethanol production methods is just the beginning of potential energy savings foreseeable from Brazilian biomass, like sugar cane.

Despite decades of gradual improvements and system optimization the standard sugar cane-to-ethanol industry can still drastically increase its NEV. This article is partly focused on acquiring accurate data related to the current practices and determining additional fossil fuel energy saving options through directed improvements. There exists a wide multitude of optimizations both on the agricultural and processing side. Before expansion into 2nd generation biofuel technology is to commence the option for improving 1st generation must be tackled first. Dehydration of ethanol into ethylene, for example, is a logical first step towards a chemical biorefinery. And as it is competing in the petrochemical industry its fossil fuel mitigation potential is higher than in the transportation fuel market[15].

In the realm of life cycle assessments (LCA) there are several terms that can be used to describe products or processes sustainability in addition to NEV. Here fossil fuel energy savings (or mitigation) is chosen and will be carried out in-depth. Relating it to the cultivated area, GJ/ha per year, will provide an indication of the sustainability per arable farmland. As fertile land is consumed by all types of biomass, edible or not, the food versus fuel issue being in favour of 2nd generation biofuels is flawed. All biomass options compete with food production, striving for the highest fossil fuel saving per land area is an additional sustainability criteria.

The BASF Eco-Efficiency analysis tool covers all ecological aspects of an LCA and several other key environmental impacts pertinent to sustainability[16]. It also takes the analysis one step further by including an economical appraisal relevant to the actual chemical industries[17]. Brazilian sugar

cane is also considered the norm in cost; in economical terms cane-ethanol is 10 – 12€/GJ. In Europe, researchers are struggling to achieve 2nd generation biofuels below 34 – 45€/GJ. Over the course of 10 – 20years worth of improvements, researchers expect the price to drop to 8.7€/GJ, thus becoming competitive to the current (standard) Brazilian biofuel[18]. In America, the pace to reach economic competitiveness of cellulose ethanol could be accelerated due to the sizeable government grants recently awarded[19]. The eco-efficiency tool ties both ecological and economical aspects together and will herein answer the question, which production option for the sugar cane is the most eco-efficient?

4.2 Calculations & Data Acquisition

4.2.1 Agricultural Input

The jargon used in the sugar cane industry when speaking about harvestable yields is *"TC"*; metric tonnes of wet cane. Typically a crop growth cycle of a 5-year period is present with each consecutive year yielding slightly less biomass, between 10 – 20%. Listed yields are averaged-out over the course of the entire cropping cycle and expressed as a yearly figure, essentially representing the 5-year cycle. Through systematic advances in agricultural procedures, cane breeding programs and a generally higher interest in efficiency, the yields have annually increased. Between the periods 1998 – 2003 the Brazilian national average was 68.7TC and by 2001 – 2005 had increased to 72.3TC[20]. The state of São Paulo had 74TC and 88TC during this time period respectively, which highlights the stress on better agricultural practice[9]. Experimental fields in Brazil have even produced in excess of 140TC per hectare annually over the growth cycle. Usina São João (USJ) which represents the higher regional average has lately yielded 103TC[21]. In the case of the sugar industry in São Paulo state the best practice yields are expected to be 125TC, indicating a feasible yield increase of 42% only through agricultural development. As the biomass sector will entail large industrial interest and large direct investment it is foreseeable that current best practice will represent the near future standard practice. Furthermore, to maximize future biorefinery schemes, collection of the cane tips and leaves (currently dubbed *trash*) can provide an extra 15tonnes fresh weight[22]. To calculate the resulting dry weight yield or useable biomass portion the exact moisture content is required. Most studies indicate a harvested moisture content of around 72 – 75% while at the USJ site the moisture content has reduced from 72.3% down to 65.7% over the past few harvest cycles[9, 21-23]. This trend of lowering moisture content to increase "TRS" (total reducible sugar) content is well-known in the industry; a final trend condition of 67.5% is representative for best practice. Table 1 provides the resulting harvestable yields and the relevant biochemical composition[9, 22, 24, 25].

To achieve the total dry weight yield of 43.5ton/ha several modifications to the standard practice must occur, especially regarding the harvesting techniques. Currently, 80% of the sugar cane fields are burnt. Recent legislation *(Decreto Federal 2661, 8-7-98 and Decreto Estadual SP 42005, 6-5-97)* is promoting a gradual ban of cane burning practices in light of local air quality and international pressures to adhere to the sustainability criteria for bioethanol export. By 2020, all

fields except those with natural barriers and obstacles (e.g. slopes above 15° and rocky areas) must be harvested raw and by 2031 all pre-harvest burning will be forbidden. The state of São Paulo is already moving in that direction with 25% of the fields currently harvested raw. The USJ site is 30%. Furthermore, trash collection can only be performed effectively using mechanical harvesting operations. Mechanical harvesting is significantly faster and more effective then manual harvesting; 2TC/day/worker versus 1200TC/day/machine. Mechanized harvesting is on the rise with currently 35% of all sugar cane collection using harvesting machines and in São Paulo it is marginally higher at 36.2%, and USJ operates at 40%. Most new and large expansion fields are mechanized, further accelerating the transition to best practice.

Table 1   Best Practice Sugar Cane Chemical Composition and Resulting Dry Weight Yields

Category	Component	Cane	Trash	Total	Total Yield
	Moisture Content (%)	67.5	80.6	68.7	ton/ha
Simple Carbohydrates	Sucrose	39.23	1.00	35.79	**15.58**
	Other Sugars	6.92	0.00	6.30	**2.74**
Complex Carbohydrates	Cellulose	19.38	38.70	21.12	**9.20**
	Hemicellulose	15.51	32.40	17.03	**7.41**
Lignin	Lignin	3.88	7.10	4.17	**1.81**
Protein	Protein	1.31	8.00	1.91	**0.83**
Fatty Acid	Fatty Acids	1.26	3.60	1.47	**0.64**
	Oils	2.95	0.20	2.71	**1.18**
Ash	Minerals	5.91	1.10	5.48	**2.38**
	Others (non-organics)	3.65	7.90	4.03	**1.76**

The employment of agrochemicals (fertilizers, pesticides, etc.) promotes the growth of biomass while preventing losses leading to high overall production yields. Sugar cane is one of the few crops in the world that has high yields and a relatively low reliance on agrochemicals. Literature on the issue of artificial fertilizer application is incoherent and simplified ranging from 245 to 470kgNPK/ha[9, 26, 27]. It is not wise to use broad data (NPK) on application rates based on averages. Individual nutrients contained in the plant are a function of the harvested yield resulting in expressing the nutrient uptake (i.e. application rates) of the crop[26]. The mature sugar cane industry has several methods to reduce the overall artificial fertilizer demand through stream recycling and clever crop rotations. The resulting artificial fertilizer demand for each nutrient is calculated by relating the nutrient uptake figures to the levels mitigated by the leguminous cover crop *(Crotalaria juncea)* and vinasse applications for the entire plantation area. Cumulative energy demand (CED) figures for each nutrient are based on best practice[28]. Table 2 lists the resulting artificial fertilizer demand and energy relation. It is claimed that pesticides are used primarily for *"corrective purposes"* and not as a default[21]. Nonetheless, the use has remained rather consistent over the last few years at around 5.0kg/ha suggesting that the same level of correction is needed[9]. Placing an increase reliance on mechanized harvesting and collecting the trash components will raise the need for pest control and no longer become corrective but standard. The CED of many major pesticides has been documented and can be grouped together based on type and related to expected application rates[29]: insecticides cost 0.96GJ/ha, acaricides cost 0.01GJ/ha, herbicides cost 1.47GJ/ha and residue pesticides account for 0.03GJ/ha.

Table 2   Overview Nutrient/Fertilizer Input Demand

Category	Macronutrients (kg/ha)						Micronutrients (g/ha)					
	N	P_2O_5	K_2O	CaO	MgO	SO_3	Fe	Mn	B	Zn	Mo	Cu
Uptake Levels	112	42	185	309	70	35	770	700	70	63	3.5	1.4
Green Manure Displacement†	50	0	0	0	0	0	0	0	0	0	0	0
Ash	0	8.3	1.4	0.2	0	0	0	0	0	0	0	0
Vinasse Displacement (70%)‡	77	30	527	241	118	202	258	774	0	258	0	258
Artificial Requirements* (vinasse fields)	0	12	0	68.3	0	0	512	0	70	0	3.5	0
Artificial Requirements (total plantation area)	18.6	21	55.4	140	21	11	589	210	70	19	3.5	0.4
Production CED (MJ/kg)	49.02	7.97	3.22	0.16	0.19	2.27	20.0					
Energy Requirements (MJ/ha)	912	136	177	22	4	24	11.8	4.2	1.4	0.4	0.1	0.01

*Plus 250kg/ha liming for pH balancing
†Standard 92 day allocation period between growth cycles: fixation of 250kgN/kg, over 5 years = 50kgN/ha
‡10-15litres (mean = 13) vinasse per litre ethanol. 8km distribution radius and 100m³/ha limit to prevent salinization

Currently, about $^3/_4$ of all sugar cane plantation in Brazil are outfitted with irrigation capabilities. Irrigation is needed when the monthly evapotranspiration (EV) is higher then the monthly effective precipitation and stored watertable combined. At the best practice yields of 125TC, the EV is 1000 – 1500mm/ha or 8 – 12mm/TC[30]. Nearly all LCA studies assess irrigation as the functional difference between these yearly EV figures and the yearly rainfall in the growth region. This is incorrect as irrigation is needed during short intervals, i.e. dry periods. A complex set of calculations parameters were used to determine the irrigation demand based on the monthly evapotranspiration for the sugar cane in the region of São Paulo and offset against the monthly effective precipitation[31, 32]. An additional 636mm/ha is needed which corresponds to 10500m³/ha of irrigation water actually applied. For reference the ferti-irrigation supplied by the vinasse is equivalent to 20.3mm/ha. To determine the corresponding cumulative energy demand the pumps are diesel supplied and operate at 6bars[33].

Each field and each plantation will follow their own specific series of cultivation and harvesting operations and will result in a distinctive relative energy consumption. As opposed to standard operations which require ca. 1500 man-hours, best practice has a full reliance on mechanical harvesters vastly lowering the human element. A general scheme can be compiled for these best practice operations with Table 3 listing the foreseen procedure and resulting energy. It is expressed as the yearly average based on the total growth cycle. Fuel consumption values are based on a predictive model with estimates on operating depth, operating width, field capacity, draft force, drawbar power and several others[34]. A neighbouring field *(viveiro)* of seedling cane is used to supply the seeding stems at a rate of 12 – 13TC/ha (12.5TC/ha). Performed once every 6 years and taking 125TC/ha yearly yields into account the land use loss is 1.67% or results in a 0.6% overall agricultural energy consumption increase.

Table 3   Cultivation and Harvesting Operations

Classification Type	Operation Name	Capacity ha/h	Fuel l/ha	Frequency* yearly factor	Energy MJ/ha
Tillage	Deep Plough	1.41	24.1	0.2	194
(Field Preparation)	Heavy Harrow	5.6	6.0	0.2	48.1
	Medium Harrow	5.6	7.0	0.2	55.8
	Light Harrow	12.0	2.8	0.2	23.4
	Fertilization	22.4	0.2	1.6	14.7
Planting	Row Furrower	11.73	2.9	0.2	23.6
	Planting Wagon	4.94	2.3	0.2	19.6
	Furrow Cover	11.73	2.9	0.2	23.6
	Pesticides	22.4	0.2	1	7.6
Harvesting	Cane Harvest	4.23	64.9	0.83	2065
	Trash Rake	10	0.4	0.83	17.6
	Trash Collection	7.45	1.9	0.83	67.4

- Performances of machines and implements under Brazilian soil conditions
- Modern medium/large tractor (New Holland TM165), modern large self-propelled harvester (Case IH 700)
- Machines lifetime: 12000hours, implements 1500 – 2000hours
- Manufacture, transportation and repair (MTR) included based on expected lifetime operation and weight
*Based on growth cycle of 5-years with 1 year for sunhemp rotation and establishment

4

Sugar cane plantations are vast with fields located in some instances more than 60km from the processing plant away. Typical plantations maintain an average transportation radius of 20km[9]; USJ has 21km[21]. Plant controlled and fed plantations plots are scattered amongst other operators; concentrating the fields in a compact area will reduce the average transportation radius to around 10km, effectively lowering the associated costs of cane transport at least half. Roads surface types vary from simple dirt roads to major highways which directly influence the diesel consumption[35]. It will be assumed that 25% of the travelled distance is dirt road, 25% by extra-urban road and 50% by highway. A wide assortment of trucks types and capacities are currently employed with an equally wide assortment of load capacities. Older trucks with single trailer capacity carry 15tons while newer trucks outfitted with triple trailers can transport as much as 80tons. Recently, Volvo introduced their 6-trailer truck-train with 180ton capacity. A best practice plantation should utilize 60ton capacity as an average.

Figure 1 presents the accumulation and provides an overview of the various categories contributing to the propagation and delivery of the sugar cane crop to the process facility. The resulting 9.1GJ/ha corresponds to 0.22GJ/tonDW biomass. Recent studies focusing on the sugar cane reveal an average agricultural energy input of 13.2 – 13.9GJ/ha or 0.69 – 0.72GJ/tonDW[9]. The above described improvement to obtain best practice lower the fossil fuel input component by a magnitude of 3.3 times, clearly indicating the increased sustainability potential.
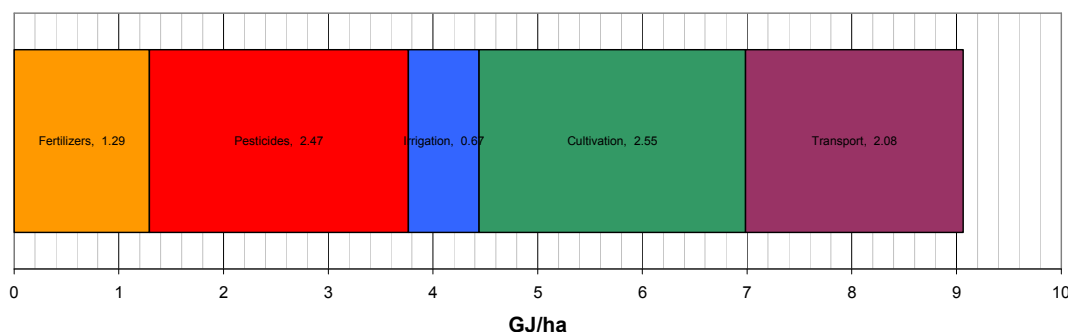
Figure 1   Agricultural Fossil Fuel Energy Input
- best practice sugar cane production

4.2.2   Factory Input

Existing processing facilities are flexible and capable of producing an arbitrary mix of crystal sugar and ethanol. The exact product ratio is market dependent as both sugar and ethanol are commodities with price fluctuations; a ratio of 50/50 is currently common. Near future implementation of the biorefinery concept for chemical production may render sugar an unfeasible co-product. In fact, most newly constructed plants are already dedicated ethanol facilities, which correspond well to the biorefinery goals. Figure 2a illustrates the process flow diagram of the milling process. The clarifier unit and filter cake by-product are not included in dedicated ethanol set-ups. Bagasse and vinasse (Figure 2b) remain in 1st generation layouts.

In standard ethanol facilities an overall cumulative sugar loss of 14.4% is present[9, 36]. The two largest sources of sugar losses (and incomplete conversion rates) are the mill train and the fermentor contributing to 3.8% and 8.9%. The fermentation reactor converts a mere 90.1% of sucrose into ethanol because most reactors are open vat systems. Conversion rates can easily be increased to 96% with little investment for closed vat systems, leading to 9.8% overall losses.

On average 16kWh/TC processed is needed to mill the canes with modern efficient systems capable of reducing it to 13.6kWh/TC[36]. Traditionally they were steam driven but are gradually being completely phased out for more efficient electric-based systems[21]. Taking the best practices into consideration, the total electric demand is 23.2kWh/TC. Nonetheless, the largest energy demand by far is the ethanol separation and purification steps. They are steam powered with an average thermal energy consumption of 330kWh/TC processed. Modern units equipped with higher pressure (and thus higher temperature) steam can reduce the demand to 300kWh/TC. Azeotropic distillation based on cyclohexane addition is still common for creating anhydrous ethanol in Brazil but is also being phased out for molecular sieve dehydration units, see Figure 2c.

The total process energy costs are primarily composed of the electric and thermal energy components, however also include indirect energy allocated from chemicals, enzymes and building materials[37-39]. The total cumulative energy input is 11.42GJ/ton EtOH. An ethanol yield

of 0.213ton/tonDW compared to the theoretic maximum conversion rate of 0.236ton/tonDW is present with 0.584ton/tonDW bagasse production.

The residual fibrous material following the mill train sugar removal step (*bagasse)* is collected and subjected to direct combustion for internal heat and power generation. Fresh bagasse has a moisture content of 48.5% (47 – 50%) and following the group contribution method for the residue biochemical components results in a calorific value of 7.18GJ/ton[28]. Drying bagasse using a conventional rotary drum drier would consume 2.4GJ/ton while yielding an extra 5.4GJ/ton of useable energy[40]. Conventional boilers operate at low pressures (21bars) with a thermal energy transfer efficiency below 60%. Modern boilers produce higher pressure steam (60 – 80bars, up to 100bars) achieving at least 78.7% efficiency[41]. Increasing the steam pressure in the facility will lead to an internal energy efficiency increase of 10%. Furthermore, the combined heat and power (CHP) production efficiency will also increase from a $16\%_{electric}$ and $63\%_{thermal}$ ratio to a 35/50 ratio. Bagasse amply covers the internal process energy requirements of the 1st generation ethanol facilities.

Large residual bagasse quantities expected and investigation into conversion techniques for bagasse-to-ethanol have commenced. Brazilian researchers have a expressed a preference for steam explosion pretreatment technology due to the abundance of available steam[36]. However, subjecting bagasse to ethanol conversion will lower the available feedstock in the CHP. Although all the unconverted material will continue to be combusted, it will no longer present excess steam. Scanning for another conversion technology with a lower energy consumption and a higher conversion rate is paramount. All technologies in the lignocellulose-to-ethanol research field are still under investigation, whether on the laboratory scale or the pilot plant scale[42]. A technology close to actual feasibility and with the lowest (calculated) energy intensity is the ammonia fast expansion (AFEX) with subsequent enzymatic hydrolysis[43, 44].

Figure 2b provides a general overview of the AFEX pretreatment system for 2nd generation ethanol production. It has recently been tested on corn distillers grains which resulted in high conversion rates and can be expected to perform equally well on other process residues, such as bagasse[45]. Whilst the actual effects have yet to be studied for bagasse, a low incomplete conversion rate of 12.4% cellulose (C6-sugars) and 22.3% hemicellulose (C5-sugars) are presumed. The residual material is collected, dried, and burnt in the CHP unit to partly displace the internal process energy. Still labelled vinasse, it contributes to the resulting oxidized waste product (ash) which distributed on the fields continues to displace artificial fertilizers.

Following a detailed NREL, Dartmouth, and the authors adjusted Aspen+ simulation model, 6.16GJ/ton of total direct energy input is required to satisfy the ethanol production from lignocellulosic feedstocks (bagasse and trash)[44, 46, 47]. Electricity contributes to 0.84GJ/ton ethanol. Unlike the milling system, electric and thermal energy do not dominate the resulting cumulative

energy. Despite the effective (proposed) ammonia recovery unit and advancement made in cellulases, the additional indirect energy allocated from chemicals, enzymes and building materials have a noticeable contribution. The total cumulative energy input is 15.04GJ/ton EtOH. An extra 0.149ton/tonDW ethanol is yielded compared to the theoretic maximum conversion rate of 0.195ton/tonDW with 0.304ton/tonDW residual (unconverted) material.

A renewed interest in producing ethylene from bioethanol has emerged in Brazil over the last few years with the recent construction announcements of two new ethylene factories[48, 49]. The dehydration of ethanol into ethylene is an easy and straightforward reaction. Investigation has shifted to solid acid catalysts such as pure silica-alumina and other zeolite configurations at a lower temperature range (180 - 300°C)[50]. Depending on the exact system and configuration the energy demand ranges from 1.8 – 2.5GJ/ton ethylene. Confidential data provided by Shell within the EU-BREW report reveals a direct energy consumption range of 0.78 – 1.15GJ/ton ethylene[51]. The cumulative energy value of 1.47GJ/ton is selected and can be considered best practice. Following the stoichiometric and conversion rates 1.66ton of ethanol is required to produce 1 ton of ethylene. A best practice biorefinery will have the ethylene synthesis capability onsite.
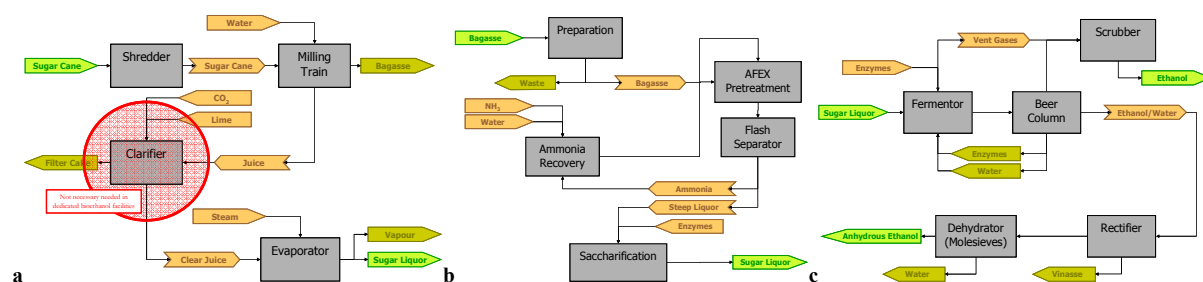
Figure 2   Simplified Process Flow Diagram for Ethanol Production
(a) cane milling (b) bagasse pretreatment with AFEX (c) ethanol fermentation and separation

4.3   Results & Discussion

In the industrial biofuel research sector and concomitant debate, common practice of data presentation and discussion towards 1st and 2nd generation ethanol technologies are segregated. Food-based versus non-food-based. This provides a convenient way to increase the contrast between the technologies and feedstocks, in many cases benefiting and supporting the validity of lignocellulosic options. In reality segregation will not occur, especially not with regards to the sugar cane. Both the sucrose and bagasse will be processed at the same facility producing ethanol and ethylene, respectively. Lignocellulosic conversion technology when applied to existing biofuel feedstocks (i.e. food-based) will act as an extension to the production capabilities. Here the mention of 2nd generation is just that, an expansion including best practice 1st generation. In the case of ethylene, 1st and 2nd are both with regards to best practice operations.

Figure 3 and 4 provide a graphical representation of the 1st and 2nd generation technology routes for ethanol used as a biofuel. All impact categories based on comparing the cumulative fossil fuel

energy demand are displayed. Pending clarification, the graphical construction description is found in a previous article[8]. Following this methodology and assessment an output energy against fossil fuel input energy (NEV) of 4.17 and 2.63 is calculated herein. Although, following traditional biofuels NEV methodology (with different boiler and biochemicals allocations) would yield 51 and 97, respectively, as indicated within the brackets. Clearly, the above mentioned improvements striving for best practice procedures on both the agricultural and processing side result in an improved net energy value, but more importantly result in a further mitigation of fossil fuels for all the impact assessment categories. A similar graph can be constructed for ethylene, instead a collection of the resulting fossil fuel saving in the various terms are presented in Figure 5. In regards to ethanol, best practice 1st generation techniques can increase the land-based mitigation potential by 340%, while expansion to include 2nd generation still outperforms the standard (average) it is however 7.5% lower then strictly 1st generation.

Ethylene production is an initial step towards a chemical biorefinery which can potentially increase the fossil fuel mitigation even further for all categories. Advanced and efficient production methods (BASF internal database) place ethylene at 67.03GJ/ton of fossil fuels, being almost entirely crude oil based[38]. This is significantly higher than the 26.8GJ/ton calorific value ethanol displaces. In figure 5, ethylene production based on the combined conversion technologies is favoured over solely relying on best practice ethanol. The different trend between ethylene and ethanol has to do with the bioenergy internally produce via the CHP. Although, an extra 22.3GJ/ton bioenergy is obtained from the 1st generation system over the 2nd generation, the mitigation potential of ethylene over ethanol is an extra 40.2GJ per ton product. Seeing that the combined route yields more product (ethylene) the overall fossil fuel mitigation potential is increased, at least for the biomass and land use categories.

The eco-efficiency assessment on the other hand contains all major environmental impact categories including, energy consumption, emissions, health effects, risk potentials, resource consumption and land use change. Figure 6 and 7 present the resulting eco-efficiency portfolios for the ethanol and ethylene systems. Assessment of the different ethanol production methods also indicate that for the normalized environmental impact best practice (BP) 1st generation is significantly more sustainable than the existing standard (average) operation and the option to expand with 2nd generation procedures. Incorporating the dehydration to ethylene leads to a greater sustainability difference between the petrochemical and biorefinery route, while still in favour of the 1st generation (BP) option. The relative difference between the BP and 2nd generation systems do decrease, while the main reason 2nd generation did not outperform BP (as the cradle-to-gate assessment stresses) is that the matrix allocation of the required resource and energy consumption figures are separated and assigned individual factors.
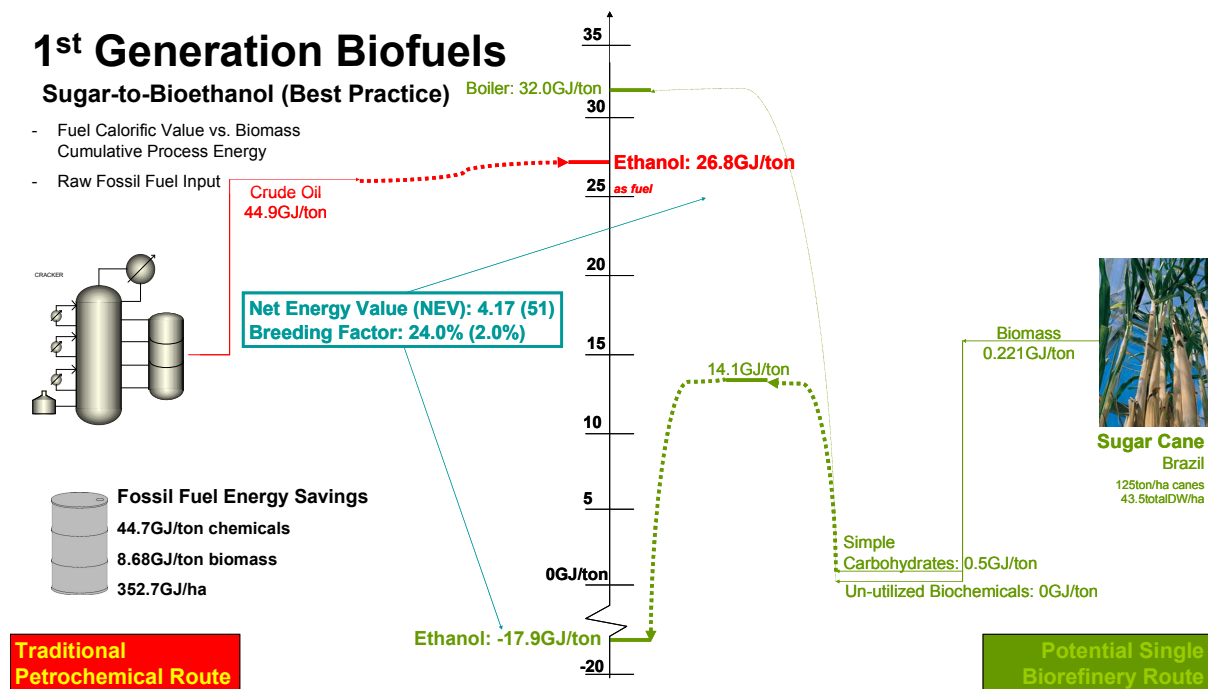
1ˢᵗ Generation Biofuels

Sugar-to-Bioethanol (Best Practice)

- Fuel Calorific Value vs. Biomass Cumulative Process Energy
- Raw Fossil Fuel Input

Crude Oil 44.9GJ/ton

Net Energy Value (NEV): 4.17 (51)
Breeding Factor: 24.0% (2.0%)

Boiler: 32.0GJ/ton

Ethanol: 26.8GJ/ton
as fuel

14.1GJ/ton

Biomass 0.221GJ/ton

Sugar Cane
Brazil
125ton/ha canes
43.5totalDW/ha

Simple Carbohydrates: 0.5GJ/ton
Un-utilized Biochemicals: 0GJ/ton

Ethanol: -17.9GJ/ton

Fossil Fuel Energy Savings

44.7GJ/ton chemicals
8.68GJ/ton biomass
352.7GJ/ha

Traditional Petrochemical Route

Potential Single Biorefinery Route

Figure 3   Pictorial Representation of 1ˢᵗ Generation Biofuels

2ⁿᵈ Generation Biofuels

Sugar-to-Bioethanol (Best Practice)
Lignocellulose-to-Bioethanol (AFEX)

- Fuel Calorific Value vs. Biomass CED
- Raw Fossil Fuel Input

Crude Oil 44.9GJ/ton

Net Energy Value (NEV): 2.63 (97)
Breeding Factor: 38.0% (0.1%)

Ethanol: 26.8GJ/ton
as fuel

15.8GJ/ton

13.8

12.2

Boiler: 9.7GJ/ton

Biomass 0.221GJ/ton

Sugar Cane
Brazil
125ton/ha canes
43.5totalDW/ha

Simple Carbohydrates: 0.14GJ/ton
Complex C6 Carbohydrates: 0.07GJ/ton
Complex C5 Carbohydrates: 0.06GJ/ton
Un-utilized Biochemicals: 0GJ/ton

Ethanol: 4.2GJ/ton

Fossil Fuel Energy Savings

22.6GJ/ton chemicals
8.07GJ/ton biomass
327.9GJ/ha

Traditional Petrochemical Route

Potential Multiple Biorefinery Route

Figure 4   Pictorial Representation of 2ⁿᵈ Generation Biofuels
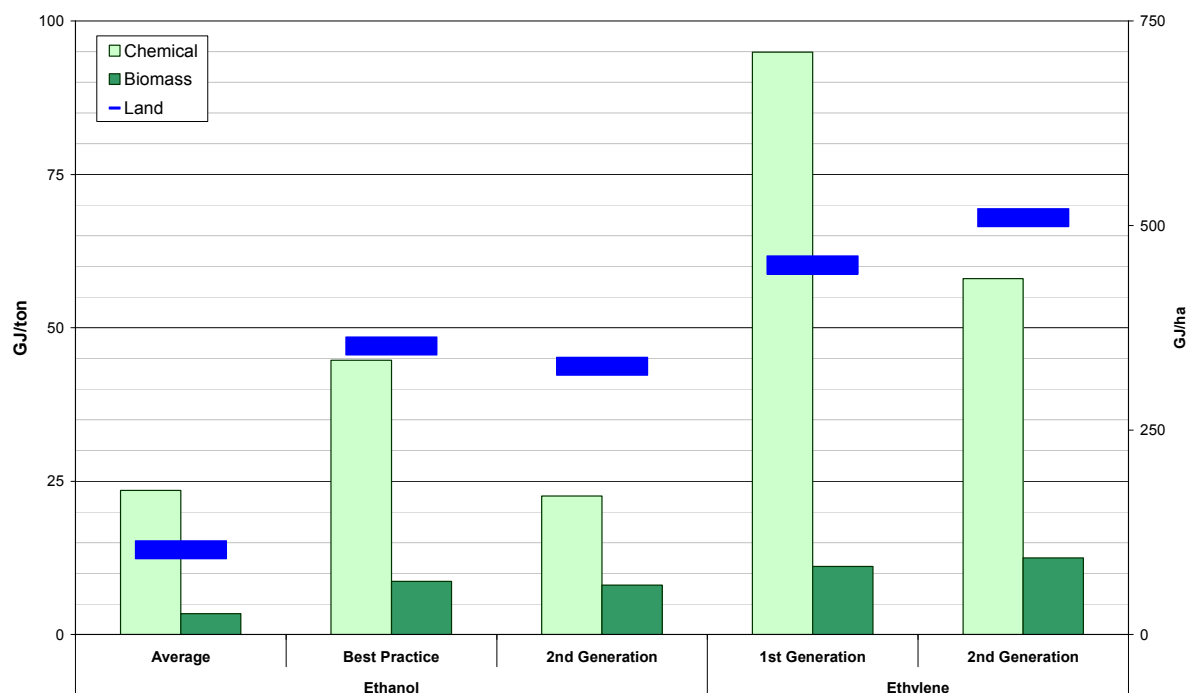
Figure 5   Comparative Overview – Fossil Fuel Energy Savings
- Ethanol yields: average = 4.7ton/ha, best practice = 8.5ton/ha, 2nd generation = 15.5ton/ha
- Ethylene yields: 1st generation = 5.1ton/ha, 2nd generation = 9.4ton/ha
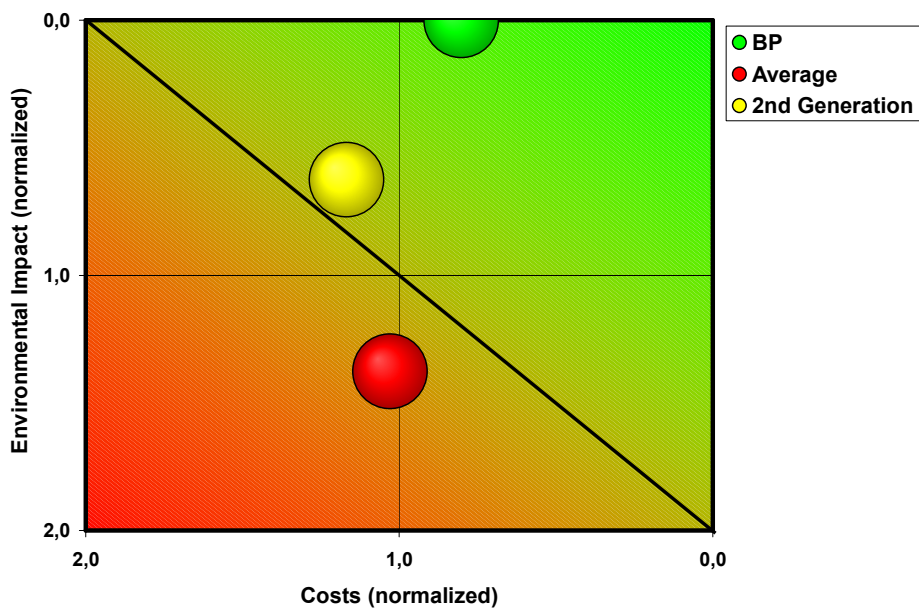
Figure 6   Eco-Efficiency Portfolio of Ethanol Production Generations
- Average: Basis - ethanol can be produced at 250€/ton internally.
- BP: best practice, extra production costs via investments up 30%, increased production volumes are 47% entailing a min. costs of 200€/ton
- 2nd generation expansion: extra production costs up 95%, increased production volume is 83% resulting in minimum costs of 265€/ton
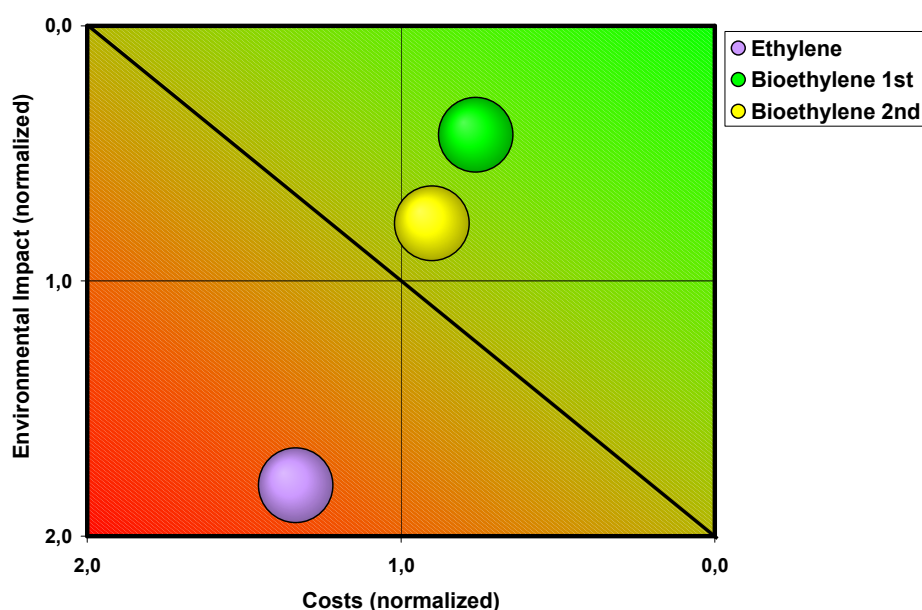
Figure 7   Figure 7. Eco-Efficiency Portfolio of Ethylene Production Generations
- Petroleum-based Ethylene: 930€/ton based on Rotterdam market prices.
- 1st and 2nd generation: previous ethanol minimum sales price plus additional dehydration equipment cost and at listed conversion rates

Ethanol can be internally produced at a minimum sales price of 250€/ton[9]. At Rotterdam ethanol has a market value of 690 – 720€/ton and ethylene 930 – 945€/ton[52]. Economically seen the potential minimum market price for all ethanol production systems are similar, although the best practice prevails. Dehydrated internally (i.e. based on minimum sales prices and not market prices) the ethylene produced from ethanol can be a very profitable venture. Overall it can be stated that best practice 1st generation ethanol and its dehydration to ethylene are the most eco-efficient.

Both the limited cradle-to-factory gate and eco-efficiency tool point towards the same conclusive results. Firstly, in the specific case on sugar cane cultivated in the Brazilian state of São Paulo, improvements of 1st generation conversion techniques are more sustainable than expansion to include 2nd generation technology. Secondly, steps towards a chemical biorefinery starting with the example of ethylene are not only more sustainable in both fossil fuel mitigation and normalized environmental impact terms, but also make economical sense.

Ethylene is the first step towards a chemical biorefinery, for residual biocomponents are sent to the CHP to be combusted. As future technologies develop and process routes mature additional chemicals and materials are envisioned from these residuals[15]. The biorefinery concept will follow a step-wise development scheme. Optimizing the current sugar cane-to-ethanol and later ethylene operations should be first on the agenda before expansion to include lignocellulosic processing is to commence.

4.4   Conclusion

The general notion arisen through the recent biofuels dispute is that industry and society would benefit from stalling biofuel adaptation based on 1st generation until 2nd generation technology developments have matured. While initially focused on a few key biomass crops, the notion has spread to encompass all biofuels, causing the general public opinion to render all 1st generation biofuels as unsustainable. The opposite is true for the sugar cane-to-ethanol production in Brazil. Improvements on 1st generation technology will lead to a more sustainable production then shifting to 2nd generation. Adhering to the food vs. fuel debate, the fossil fuel mitigation potential for the various biofuel and biochemical production routes were determined per cultivated land area. Fertile land is consumed and occupied by all biomass crops, the biomass option with the highest mitigation potential per land can be considered to be not only most sustainable but also least intrusive to food production. Standard (average) bioethanol production displaces an already impressive 104GJ/ha/a. A detailed report following a similar methodology for various types of biofuel documented a staggering 150 – 200GJ/ha/a fossil fuel energy savings for the Brazilian sugar cane-to-bioethanol, which is the highest recorded thus far in literature[53]. Nonetheless, listed improvements to best practice operations more than double the savings to 353GJ/ha/a beyond the 328GJ/ha/a attainable through the inclusion of 2nd generation conversion. Early steps towards a chemical biorefinery, such as ethanol dehydration to produce ethylene, can increase the land-based fossil fuel savings up to 509GJ/ha/a. BASF's eco-efficiency tool validated these specifically directed findings by providing an overview of the total environmental impacts with similar results. Independently the results offer an insight into the chemical industry's potential acceptance of products derived from the biobased economy. The most logical step environmentally and economically is first the improvement of the existing 1st generation operations and secondly the eventual expansion into the production of ethylene. The field of biomass is regionally dependent and complex with a vast array of potential products. It is all too easy to criticize and generalize, the biobased economy deserves highly specific assessments.

4.5   Acknowledgements

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Chapter 5

Improving the Corn-Ethanol Industry:
Studying protein separation techniques to obtain higher value
added product options for distillers grains

5

Abstract

Currently in America the biofuel ethanol is primarily being produced by the dry grind technique to obtain the starch contained in the corn grains and subsequently subjected to fermentation. This so-called 1st generation technology has two setbacks; first the lingering debate whether its life cycle contributes to a reduction of fossil fuels and the animal feed sectors future supply/demand imbalance caused by the co-product dry distillers grains (DDGS). Additional utilization of the cellulosic components and separation of the proteins for use as chemical precursors have the potential to alleviate both setbacks. Several different corn feedstock layouts were treated with 2nd generation ammonia fibre expansion (AFEX) pre-treatment technology and tested for protein separation options with solvent extraction and protease solubilisation. The resulting system has the potential to greatly improve ethanol yields with lower bioprocessing energy costs and satisfy a significant portion of the organic chemical industry.

Keywords

AFEX, Ethanol, DDGS, Wet Cake, Protein, Protease, Acrylonitrile

5.1 Assessing the Problem

5.1.1 *Fossil Fuel Reduction*

Each country, and to an extent region, has their own way of looking at the lingering dilemma of finite fossil fuels supply and the environmental burden associated with their use. Fermenting carbohydrates contained in biomass into ethanol is one of the aspirations of American and other nations' political leaders and academia to reduce dependence on foreign oil[1, 2]. Environmental concerns such as greenhouse gas emissions which are raising on the national agenda are fortuitously reduced as direct and indirect fossil fuel usage are avoided. Producing ethanol from biomass crops such as corn is not fossil fuel energy or carbon dioxide free as commonly understood. Energy, and thus emissions are required throughout the production chains in many indirect forms such as diesel for tractors, natural gas for fertilizers, heat and power (coal) for bioprocessing, etc. Currently, ethanol is produced via dry grind and wet milling technologies based on the starch content of corn grain. A score of reports and articles have been produced listing the energy and to a limited degree environmental aspects of producing ethanol from such technologies[3]. These studies are the source of debate as particular individuals indicate a negative energy value, meaning that more fossil fuel energy is required than mitigated. This is a common argument when assessing the so-called 1st generation ethanol plants, while others argue that the chosen metrics employed in energy efficiency assessments, particularly that of "net energy", are flawed and must be reassessed[4]. Nevertheless striving for the maximum savings of fossil fuels requires the utilization of the entire crop components (not merely the starch of the cobs) and the newer technology associated with it. Once the economic profitability issues have been satisfied the ethanol industry should set its goals at achieving the highest possible reduction of fossil fuels and increase its renewable resource status.

5.1.2 *Co-Product Devaluation*

As of 2006 there were 110 operational ethanol plants in the USA with a total production capacity of 16.40Mton, of which 82% of the capacity were built utilizing the dry grind technique[5]. A major co-product of these production facilities is dried distillers grain with solubles (DDGS) which is used as a valuable animal feed; 75-80% ruminants, 18-20% swine and 3-5% poultry. It is produced in vast quantities, over 10.0Mton in 2006 as just under 1kg DDGS is produced per kg ethanol with the dry grind process. According to the U. S. Renewable Fuels Standard (RFS) of 2005 it is expected that by 2012 22.39Mton of ethanol and 12-14Mton of DDGS will be produced. This poses a problem for the industry as the selling price of DDGS is rapidly decreasing: $145/ton in 1980 to $67/ton in 2005 without even taking inflation into account[6]. The entire domestic compound feed industry is roughly 150Mton with 42Mton allocated to the cattle sector[7]. As more ethanol plants become operational the magnitude of DDGS will saturate the market and is expected to cause the market prices to fall even further. On the other hand, DDGS could stabilize at a price reflective of its feed utility with respect to corn. At this point, DDGS would essentially be valued as a corn substitute and no further price drop would occur.

However, the current drop in price does affect the overall economics of ethanol and could put the entire industry in jeopardy, much like glycerol did with biodiesel in Europe[8]. Other higher value added products need to be found for the by-products to maintain their co-product status. Ideally the product would also contribute to the reduction of fossil fuels further supporting the renewable image.

5.1.3 *Aim of the Paper*

The biobased economy is emerging as a pivotal topic and is generally regarded as reaching large-scale implementation in the very near future. Already 1st generation corn-to-ethanol plants are built and operating across the United States of America, but use only the starch portion of the crop and produce vast quantities of distiller grains as a by-product. AFEX technology enables an additional quantity of ethanol to be produced from the by-product and with downstream protease treatment a respectable quantity of proteins/amino acids can be separated and isolated for use as chemical precursors. Furthermore, considering optimal process integration the most logical state of the by-product has revealed that using distillers grains directly from the column is not only feasible but energetically advantageous. The aim of this paper is to indicate possible improvement options for the existing ethanol industry and help guide future research directions.

5.2 Materials and Methods

5.2.1 *Feedstock Choice*

Upon harvesting the crop corn is separated into two basic parts; the kernel (grain) portion of the ears and the residual stover. As mentioned the current ethanol industry uses the starch-rich portion of the grain as its feedstock. The rest of the components in the grain are collected, dewatered and become Dry Distillers Grain with Solubles (DDGS). DDGS contains residual carbohydrates (starch, cellulose and as well as other polysaccharides) that might potentially be converted into fermentable sugars. The "D" for dry connotes that the waste stream of the ethanol distillation column is originally wet. In fact, prior to drying the grains have a moisture content in the vicinity of 65%. This material is technically referred to as wet distiller's grains but the colloquial wet cake (WC) is common and will be used herein. The ability to use the wet cake as a feedstock has an energetic advantage by mitigating the drying costs:

- 2926kJ/l ethanol (10500BTU natural gas per gallon ethanol, EPA) with 1.069kg wet cake/kg ethanol → 2.47GJ/ton wet cake dry weight

The other part of the corn, stover, is one of the commonly mentioned options as a source for lignocellulose. In a truly integrated system both the stover and the wet cake would be combined and subjected to the same pretreatment. The ratio between the two streams must match the amount produced by the crop (excluding the central wooden core, corncob):

- Ear: 20.6% moisture (upon harvest), 20%wet weight of corn plant
- Stover: 45% moisture (upon harvest), 80%wet weight of corn plant, 10% moisture (delivered) → Upon Harvest: Ear = 26.5% dry weight, Stover = 73.5%

- Wet Cake: 64.7% moisture (delivered), 55%dry weight of ears → Delivered (fresh feedstock weight) Mix = $^1/_3$ wet cake, $^2/_3$ stover

The DDGS and WC were obtained from Big River Resources (West Burlington, IA), the corn stover was obtained from NREL (Golden, CO) and the gluten meal was obtained from a local animal feed distributor. The feedstocks to be assessed are stover, wet cake, the wet cake and stover mix, DDGS and gluten meal with their corresponding chemical compositions listing in Table 1. The exact values were derived from in-house knowledge, Purdue University analysis and external testing at the DairyOne Forage Laboratory[9]. For later calculations using Aspen[+] simulation models the corresponding *"aspen components"* are needed and have been adjusted accordingly, differing slightly from the standard nutritional chemical composition. For example, under simple carbohydrates (CH) galactose and mannose are used to represent the behaviours of starch in the simulation program. For these experiments however, the complex C6 (i.e cellulose) and simple carbohydrates (i.e. starch), and the protein levels are of interest. The energy content values are based on the group contribution method for each of the individual components with only the results listed[10]. Gluten meal was chosen as a base feedstock for the protease experiments as the protease was developed for gluten proteins, mentioned in detail in a later section.

Table 1   Feedstock Chemical Composition

Aspen Components	Biochemical Components	Stover	Wet Cake	Wet Cake + Stover	DDGS	Gluten Meal
Galactose	Simple CH	0.009	0.0125	0.010	0.0125	0.2
Mannose		0.003	0.0125	0.004	0.0125	0.191
(Cellulose) Acetate	Complex C6	0.037	0.0213	0.034	0.0213	0.001
Cellulose		0.317	0.134	0.287	0.134	0.009
Soluble Solids		0.030	0.0313	0.030	0.045	0.001
Arabinose	Complex C5	0.028	0.027	0.028	0.027	0.005
Xylose		0.210	0.125	0.196	0.125	0.015
Lignin	Lignin	0.181	0.025	0.155	0.025	0.019
Protein	Protein	0.063	0.339	0.109	0.324	0.470
Extract	Fatty Acids	0.043	0.107	0.054	0.107	0.018
Ash	Ash	0.030	0.0313	0.030	0.045	0.001
Undetermined	N/A	0.0	0.080	0.013	0.080	0.0
Moisture	H_2O	0.10	0.647	0.190	0.112	0.082
Energy	GJ/ton	16.6	17.6	16.8	17.7	15.9

- Do not necessarily correspond directly to actual chemical composition, adjusted for simulation component types
- Dry weight basis, kg/kg

5.2.2   AFEX

5.2.2.1   Background and Reasoning

Many pretreatment options exist to better facilitate the enzymatic hydrolysis prior to fermentation. Without pretreatment the densely-packed and rigid crystalline cellulose structure is resistant to enzymatic hydrolysis. At Michigan State University (MSU) a novel physiochemical pretreatment known as Ammonia Fiber Expansion (AFEX) or in older articles "Explosion" has been developed and patented[11]. By supplying ammonia under pressure (0.65 – 3.5MPa) and moderate temperatures (70 - 150°C) for a short residence time (5 – 15min) the ammonia can

permeate and react with biomass components. Upon a quick release of pressure the biomass structure is broken apart causing various degrees of lignin solubilisation, hemicellulose hydrolysis, cellulose decrystallization and more notably an increased surface area[12].

Considering the high degree of variability of conditions dependent on each biomass feedstock the energy demand can swing considerably. But the recovery and recycling of ammonia remains the main driver of the high energy costs[13]. It is however proposed that a cold water quench system as opposed to the traditional evaporation tank and condensation system can greatly reduce the ammonia recovery and recycling costs[14]. One concern for the success of the system is the ability to add hydrous ammonia (NH_4OH) in place of anhydrous ammonia. The optimal AFEX conditions for corn stover was thoroughly investigated and hydrous ammonia under particular temperatures worked best[12]. Similar optimisations for other feedstocks have been conducted in particular for wet and dry distiller's grains[15]. All the feedstocks herein were subjected to identical AFEX pretreatment with the hydrous ammonia medium under the following operation conditions:

- 90°C, ~0.75MPa, 1:0.3:0.25 (Biomass:Ammonia:Water), 5 minutes residence time

5.2.2.2   Procedure

In a 300mL stainless steel pressure vessel the right mixture of feedstock and water was added. To adhere to the reactor design only a limited amount of biomass (20g dry weight) can be added necessitating glass marbles to fill the void space and reduce the amount of ammonia in the vapour phase. After the lid was bolted closed the reactor was charged with the appropriate amount of premixed hydrous ammonia. Using a 400W PARR heating mantle the room temperature reactor was heated for 15 to 20 minutes bringing the contents to the desired temperature (90°C) and additionally held for the required residence time (5 minutes). Quickly opening an exhaust value rapidly released the pressure. As the ammonia recovery system has not yet been fully researched and does not exist on a laboratory scale, the samples were removed and placed under a fume hood overnight to remove residual ammonia.

5.2.3   *Enzymatic Hydrolysis*

The National Renewable Energy Laboratory protocol LAP-009 was followed[16]. Firstly all the biomass was placed into a 1000mL Erlenmeyer flask. To equal a 1.2% total glucan/water solids loading, autoclaved water was added accordingly and buffered to pH 4.8 using 15 – 20mL 1M citrate buffer. Specyme CP (Genencor, Palo Alto, CA) cellulase was loaded at 15FPU/g glucan and β-glucosidase (Novozyme 188, Bagsværd, DK) at 56NPGU/g glucan. In these sets of experiments no xylanase was added, as particular xylanase enzymes and levels have yet to be optimized. Incubation occurred at 50°C at 200rpm rotation for 5 days. The long residence time was chosen to ensure the maximum conversion.

5.2.3.1 Sugar Analysis

A series of 6 tests were conducted for all the feedstocks with 2 additional test runs for the DDGS and WC feedstocks by using a collection of 1mL liquid samples which were prepared from the post hydrolysis liquid stream. The analysis was done using a Water High Performance Liquid Chromatograph (HPLC) system equipped with a Bio-Rad (Richmond, CA) Aminex HPX-87P carbohydrate analysis column. At a constant 85°C, degassed HPLC water with a flow rate of 0.6mL/min was used as the mobile phase. The fermentation step was not conducted in this set of experiments. Many other fermentation tests have been conducted on AFEX/enzyme treated material revealing a glucose and xylose to ethanol conversion rate of approximately 95%[12].

5.2.3.2 Protein Analysis

Each of the post hydrolysis liquid samples were also tested for protein content. The samples were diluted 10-fold and tested using the Pierce Assay Kit (Thermo Fisher Scientific Inc., Rockford, IL). Peptide bonds in proteins react with the BCA (bicinchoninic acid) agent changing the solution's colour from green to violet that absorbs light at 540nm. All the samples were prepared in a microplate and incubated for 30minutes at 37°C. The colorimetric analysis was performed in the Bio-Rad absorbance reader (Richmond, CA) Model 680XR.

5.2.4   Protease Digestion

5.2.4.1 Background and Reasoning

The field of biotechnology is emerging as a very promising alternative to the traditional chemical process options. Industrial proteases are enzymes specially designed, usually genetically tailored, to effectively break down peptide bonds of proteins. This mechanism is called peptide cleavage and occurs at specific activation conditions. Genencor (Leiden, NL) developed a thermostable bacterial neutral metalloendopeptidase derived from a select strain of *Geobacillus sp. (rokko)* which has been marketed as Protex 14L. It is claimed to efficiently hydrolyse a wide variety of protein substrates, mainly food grade sources, and was intensively tested with wheat gluten. At 160units/g the working conditions were found to be in the range of pH5.0 – 9.0, 35 – 80°C and a loading of 0.1 – 1.0% formulation **w**eight versus the **w**eight of the protein in the substrate. For wheat gluten the optimal conditions were pH7.5, 72°C with a loading of 0.75%w/w. As each peptide bond is cleaved a water molecule is required meaning the reaction occurs in aqueous solution with typical solid loading rates below 10%. Corn, in particular corn stover proteins, were not amongst those protein substrates tested by Genencor meaning the optimal conditions (temperature, pH, loading, time, etc.) need to be determined and brought into relation with their respective energetic costs.

5.2.4.2 Procedure

Placed into 250mL Erlenmeyer flasks was 2.5 grams of the solid stream biomass (dry weight basis). A representative solid/liquid loading of 5% was chosen by adding 50mL of deionised water. The acidity of the samples was measured and recorded. One set of experiments left the

acidity as is, whereas by using 10mL of a 1M Tris (2-amino-2-(hydroxymethyl)propane-1,3-diol) and hydrogen chloride solution the other ones were buffered at pH7.5. For each set of tests two loading conditions were prepared, 0.1%w/w and 1.0%w/w with the required protease volumes determined by the results of the post-hydrolysis protein levels in the feedstock. The samples were placed in the rotational incubator at different temperatures: 40°C, 50°C and 72°C and for various time periods: 6, 12, 24 and 120hours. The speed of rotation was 200rpm.

5.2.5   *Protein Content Analysis*

Protease digestion has the capability of breaking down the polypeptides to a few bonds and even down to the basic free amino acids. Such small molecules are beyond the detection range of the Pierce Assay for it has a specific lower size limit of 6kDa[17]. Considering that free amino acids have an average size of 0.110kDa the minimum detectable polypeptide size is about 50. The Pierce Assay was used on all samples to further elaborate on the degree or proportion of peptides below 6kDa. To detect the level of smaller peptides two analysis methods were employed; nitrogen content and amino acid content analysis. The chemistry department of MSU were contracted to perform both analytical methods; the nitrogen content was performed by means of combustion with a carbon, hydrogen, oxygen and nitrogen emission gas analyser and the amino acid content was performed using an HPLC after complete sulphuric acid hydrolysis. By factoring in 6.25gProtein/gNitrogen the total protein/amino acid content of the samples can be determined from the nitrogen content method. The amino acid analysis was used sparingly due to the high associated costs; it was employed for all the feedstocks on the 72°C/24hours batch of samples with the primarily purpose of validating the nitrogen content method. At the low solids loading and resulting low concentration in the tested liquid streams, the nitrogen content analysis was close to the lower limits of the apparatus. Unfortunately the figures for 72°C/120hours/7.5pH and 50°C/120hours/5.3pH were below the lower limit. Due to the reduced accuracy accompanying the low concentration detection range a few test results gave protein solubilisation values well over 100%. These results are not completely useless because a clear correlating trend is observable when compared to the amino acids analysis conducted on the same streams. Using the correlation trend the nitrogen analysis figures above 100% were adjusted accordingly. In such cases, the larger of the two protease loading figures was set at 95% while the other one was reduced using the relative proportionality of the nitrogen analysis pair. Mass spectrographic analysis was also performed using a Waters Quattro-Micro API system (Milford, MA) on two repeat samples of the DDGS and WC at the 50°C condition as an additional method of validity. Samples were first hydrolyzed to their resulting amino acids in a 6M solution of HCl at 110°C for 24 hours. Valine-d8 was used as an internal standard. Due to the poor resolution of some amino acids, only selected amino acids were used in the final analysis under the assumption that similar treatments of the same feedstock would produce similar amino acid profiles (see Figure 1).

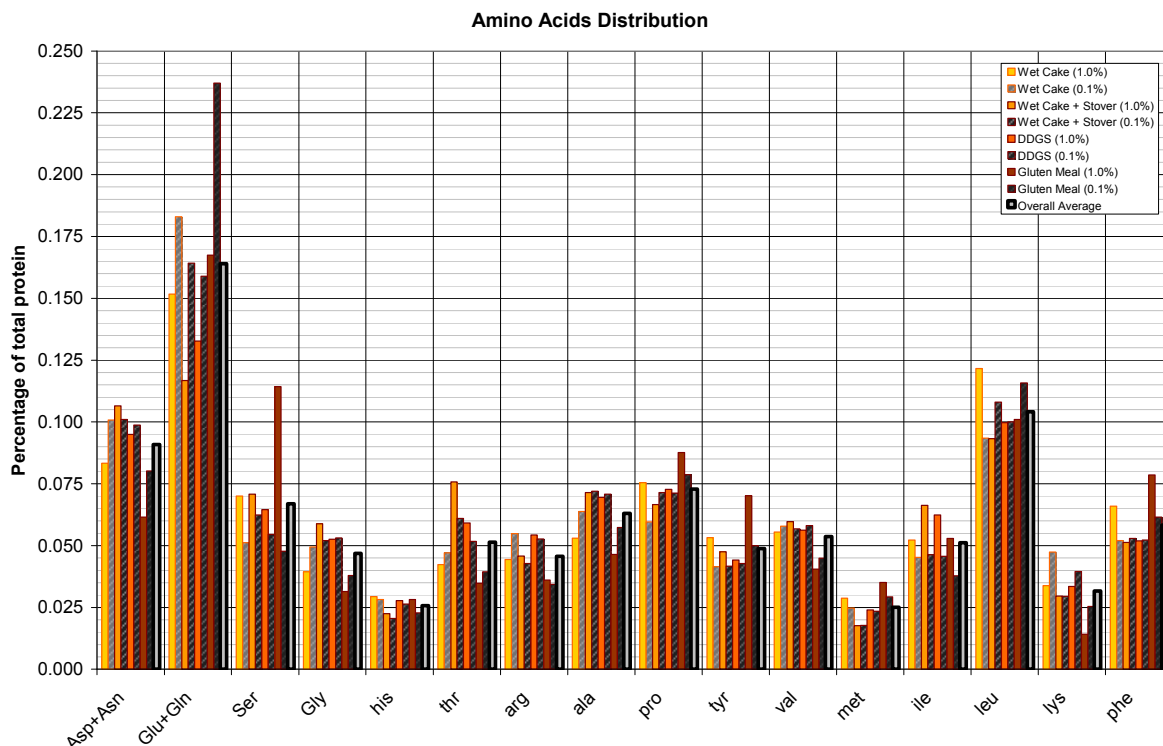**Amino Acids Distribution**

Figure 1   Amino Acid Distribution of Protease Digested Corn Protein

5.3   Results

5.3.1   Sugar Conversion Rates

Some of the measurements fell outside of the 3-σ range and were discarded in assessing the mean conversion rates. The resulting C6 carbohydrate conversion rates were:

- Stover: 87.4 – 98.2% (mean 94.1±5.96%)
- Wet cake: 62.9 – 83.0% (mean 74.0±10.3%)
- Wet cake + stover: 91.0 – 97.0% (mean 94.9±2.8%)
- DDGS: 86.4 – 94.8% (mean 91.3±4.4%)
- Gluten meal: 87.5 – 96.0% (91.4±6.8%)

A conversion rate of 100% corresponds to a complete conversion of the glucan content contained in the feedstock (listed as the Aspen[+] components galactose, mannose, acetate, cellulose and the soluble solids) into glucose with the correct stoichiometric adjustment of 0.90gC6/gGlucose. Although xylanase was not added stover had a C5 carbohydrate polymer conversion rate in the range of 65% whereas the distillers grains (being the lowest) still had 12.5% C5 polymer conversion. The trace xylanase activity is mostly attributed to the commercial impurities of the cellulase enzyme formulation. It will however be assumed that the proper configuration will shortly be found and that the C5 conversion rate will match that of the C6.

5.3.2   Base Protein Conversion Rates

The influence of glucose and residual ammonia on the BCA agent were individually measured, taken into account and deducted from the end values. However, soluble lignin also affects the results by bonding to the BCA agent. AFEX/enzymatic pretreatment is known for solubilizing lignin and in a slightly different ammonia reactor setup a rate of 70% delignification was observed[18]. Delignification is the break down of the complex lignin structure into its smaller components (aromatics), however the rate of delignification does not necessary correspond completely with the level of solubilization as some of the smaller lignin components can remain insoluble. Dilute acid pretreatment, which also causes delignification, it is known to solubilise lignin at the rate of 33%[19]. Thus approximately one third of the lignin is solubilized and ends up in the liquid phase; this value will be taken into account herein. Obtaining purified solubilized lignin from biomass samples is hard if not impossible to acquire, which could be used to offset the reactive influence on the BCA agent of the Pierce Assay. Furthermore lignin's unique structure is chaotic, yielding a wide variety of different aromatics that will all interact independently with the BCA agent. Manually adjusting the Assay's value by including the solubilisation portion was performed. By interlinking all the experimental data results into a calculation matrix the best correction factor for lignin's influence on the BCA agent was determined; 2.75 was found to provide the most realistic values. It is however advised that this correction factor be independently validated using a purified solubilized lignin stream, for future BCA studies on high lignin containing biomass.

The purpose of the measurements is to determine the amount of protein left in the solid stream after the pretreatment stage by quantifying the level in the liquid stream. The protein in the residual solid phase is the total amount available for subsequent treatment/separation. The lost portion contained in the liquid phase will end up being partly digested by the fermenting micro-organism (lowering the nutrient demand) and will eventually be combusted in the combined heat and power unit; finally yielding the calorific value. As with the hydrolysis data a select few data points fell outside the 3-σ range and were discarded in assessing the mean protein levels. The initial protein content of the feedstock is known (Table 1) and by relating the residual solid phase dry weight to the determined protein concentration in the liquid phase the resulting proportions of the protein solubilized/lost can be determined:

- Stover: 22.3 – 45.3% (mean 35.2±11.8%)
- Wet cake: 32.7 – 41.2% (mean 37.7±3.6%)
- Wet cake + stover: 26.9 – 44.5% (mean 38.3±9.9%)
- DDGS: 17.6 – 26.0% (mean 22.4±2.9%)
- Gluten meal: 35.3 – 42.1% (38.4±4.2%).

Thus the resulting mean protein concentrations in the solid phase feedstock were; stover: 10.2%, wet cake: 47.5%, wet cake + stover: 18.2%, DDGS: 52.9%, gluten meal: 70.8%.

5.3.3 Protease Protein Digestion

Protein solubilities (source: nitrogen content/mass spec), the small peptide proportion (source: Pierce Assay) and the overall yields per ton dry feedstock are listed in Table 2 – 6. The *protein solubility* figures indicate the percentage of the total protein content in the post-hydrolysis solid stream feedstocks that have been solubilized; the *small peptide proportion* figure represent the quantity of these solubilized proteins that have been cleaved to below 6kDa particle size; the *soluble protein yield* lists the solubilized protein content in relation to 1ton dry feedstock from the start of the entire process chain. The main feedstocks of investigation are the DDGS and WC as can be seen by the larger abundance of data and an extra set of experiments were conducted at 50°C, pH7.5 for both loadings with additional measurements at the 6th and 12th hour (Figure 2).
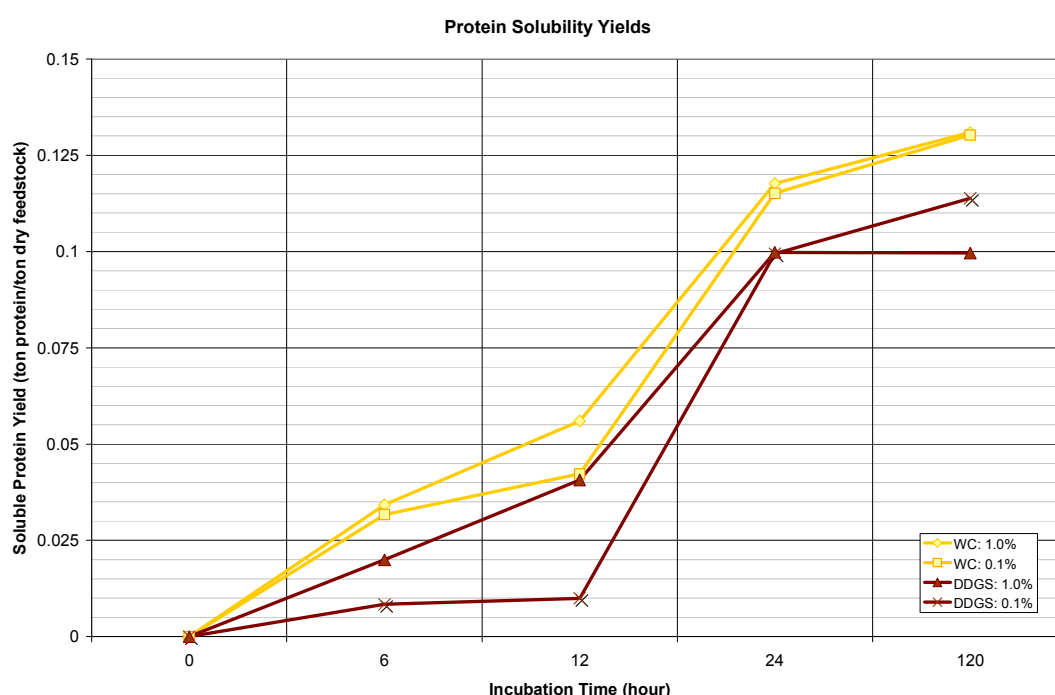
Figure 2   DDGS and WC Protein Solubility Yields at 50°C/pH7.5 Protease Digestion

As can be seen from both the figures and the graphs most of the protein digestion happens between the 12th and 24th hours. In fact, the tests at 120hours were probably overly pessimistic and not essential as Genencor product information sheet indicates the initial digestion progress for the first 3 hours only, suggesting that most of the protein cleavage occurs in the course of a few hours. Only in a select few settings/conditions does 120hours yield noticeably more soluble proteins than 24hours. Considering Genencor operates their investigations based on pure feedstock streams it is understandable that the complex biomass feedstocks and the residual unsolubilized protein portion require longer residence times to attain the bulk of the peptide cleavage. All of the data listed in the tables refer to the runs at pH7.5. The acidity of the unaltered streams was in the vicinity of pH5.3. In all cases the solubilisation performed significantly worse with an uncontrolled pH. The level of total solubilized proteins was for the large part well below

50%, with DDGS at 0.1%w/w (protease/protein) reaching 63% after 120hours. However, more striking is that for most of the feedstocks around 95% of the solubilized proteins were smaller than 6kDa. This would suggest that under such conditions either the ends were attacked leaving the residual protein still insoluble or that the proteases act locally attaching and digesting one protein molecule until completion (i.e. below 6kDa) before spreading leaving many molecules intact. As a concluding statement regarding acidity, it is imperative that a pH level of 7.5 is maintained. Other optimal conditions and trends are discussed separately for each feedstock.

5.3.3.1 *Stover*

Table 2   Stover Protease Protein Solubility

Protease Residence Time	h	24			120		
Protease Temperature	°C	40	50	72	40	50	72
Protein Solubility (1.0%)	%	40.0	43.4	84.4	95.0	94.7	95.0
Small Peptide Proportion (1.0%)		10.0	52.8	22.9	5.0	11.9	10.0
Protein Solubility (0.1%)		90.0	95.0	95.0	86.6	95.0	95.0
Small Peptide Proportion (0.1%)		5.0	5.0	34.5	60.1	5.0	50.0
Soluble Protein Yield (0.1%)	ton	0.016	0.018	0.034	0.039	0.039	0.039
Soluble Protein Yield (1.0%)		0.037	0.039	0.039	0.035	0.039	0.039

For stover in particular all of the nitrogen analysis values, in absolute terms, are above 100% meaning the figures were adjusted using the correlation trends. This places a great deal of uncertainty on this particular feedstock as the effect of lignin needs to be further invested, comprising 18.1% of the feedstock dry weight. Already with the determination of the solubilized protein content after hydrolysis a standard deviation of 11.8% was found, compared to those of the lower lignin feedstocks being below 5%. From the trends however, a near complete solubilization is noticeable for most tested conditions. Time is a major factor, not in the total protein solubility but in the breakdown into smaller peptides. Periods above 24 hours would be beneficial for continued peptide cleavage, whereas only minor positive trends are noticeable at increased temperatures and loadings, meaning low temperatures (40°C) and loadings (0.1%w/w) perform adequately so long as the residence time is sufficient.

5.3.3.2 *Wet Cake*

Table 3   Wet Cake Protease Protein Solubility

Protease Residence Time	h	6	12	24			120		
Protease Temperature	°C	50	50	40	50	72	40	50	72
Protein Solubility (1.0%)	%	16.2	26.5	70.0	55.7	64.8	83.0	61.9	62.8
Small Peptide Proportion (1.0%)		75.0	78.0	95.0	86.4	91.1	78.4	89.3	73.8
Protein Solubility (0.1%)		15.0	20.0	65.0	54.5	54.9	67.7	61.6	46.5
Small Peptide Proportion (0.1%)		70.0	72.5	95.0	89.0	92.0	88.1	84.3	84.2
Soluble Protein Yield (1.0%)	ton	0.034	0.056	0.148	0.118	0.137	0.175	0.131	0.133
Soluble Protein Yield (0.1%)		0.032	0.042	0.137	0.115	0.116	0.143	0.130	0.098

It is imperative that the protease is allowed to digest for at least 24hours, whereas periods past 24hours present a minor additional effect. At the long residence times (120hour) the overall protein solubility rate does slightly increase by 5 – 10% while the small peptide proportion decreases by 5 – 10% suggesting that the additional proteins brought into solubility are larger peptides only partly cleaved. The same is true for the temperature dependence, with 10% higher rates at 72°C over 50°C with the difference between 40°C and 50°C being much lower. A slight leading toward better digestion is observable at higher loading conditions and does initially accelerate the process, although by merely a few percent suggesting that lower levels are possible. For all conditions the vast majority of the solubilized proteins are small peptides, in the range of 85-90%.

5.3.3.3   Wet Cake + Stover

The proportion of stover in the mix is predominant and that is clear in the response to the protease. Again the values indicate the influence of the lignin portion of stover as the compensation method again needs to be included to match the trend. In contrast to stover alone, the solubility is slightly lower while the small peptide proportion is higher, as expected in consideration of the wet cake contribution. Higher temperature appears to have a negative influence and the lean towards the lower loadings is more apparent.

Table 4   Wet Cake + Stover Protease Protein Solubility

Protease Residence Time	h	24			120		
Protease Temperature	°C	40	50	72	40	50	72
Protein Solubility (1.0%)	%	95.0	95.0	68.0	94.7	90.4	24.4
Small Peptide Proportion (1.0%)		25.0	52.9	77.2	7.0	11.8	32.6
Protein Solubility (0.1%)		95.0	95.0	95.0	95.0	95.0	29.7
Small Peptide Proportion (0.1%)		95.0	95.6	5.0	4.3	18.4	46.2
Soluble Protein Yield (1.0%)	ton	0.063	0.063	0.045	0.063	0.060	0.016
Soluble Protein Yield (0.1%)		0.063	0.063	0.063	0.063	0.063	0.020

5.3.3.4   DDGS

Table 5   DDGS Protease Protein Solubility

Protease Residence Time	h	6	12	24			120		
Protease Temperature	°C	50	50	40	50	72	40	50	72
Protein Solubility (1.0%)	%	10.0	20.4	60.0	50.0	47.5	80.0	49.9	82.6
Small Peptide Proportion (1.0%)		98.0	98.0	99.0	98.1	97.0	75.0	90.0	89.6
Protein Solubility (0.1%)		4.2	5.0	55.0	49.9	47.3	67.8	57.1	95.0
Small Peptide Proportion (0.1%)		97.0	98.0	99.0	98.6	97.4	91.6	89.4	85.8
Soluble Protein Yield (1.0%)	ton	0.020	0.041	0.120	0.100	0.095	0.189	0.100	0.165
Soluble Protein Yield (0.1%)		0.008	0.010	0.110	0.099	0.094	0.135	0.114	0.189

The response to protease digestion is the slowest amongst the tested feedstocks. At 24hours the solubility levels are rather consistent, producing a range of 47.3 – 60% and annulling any major

influence of temperature and loading levels. However, at long residence times and high temperatures (120hours and 72°C) the solubilization value are at near completion. Furthermore, of the solubilized proteins, the small polypeptides are in the high 90's suggesting that of the attacked proteins the cleavage occurs over the entire molecule.

5.3.3.5 Gluten Meal
Table 6   Gluten Meal Protease Protein Solubility

		24			120		
Protease Residence Time	h						
Protease Temperature	°C	40	50	72	40	50	72
Protein Solubility (1.0%)	%	75.0	70.9	61.6	47.9	44.8	54.1
Small Peptide Proportion (1.0%)		97.0	96.8	92.5	91.4	99.7	79.1
Protein Solubility (0.1%)		40.0	37.9	34.8	95.6	95.0	59.0
Small Peptide Proportion (0.1%)		65.0	75.1	84.7	82.0	80.7	88.8
Soluble Protein Yield (1.0%)	ton	0.274	0.259	0.225	0.175	0.163	0.197
Soluble Protein Yield (0.1%)		0.146	0.138	0.127	0.349	0.347	0.215

Protex 14L was developed for food grade proteins and tested on wheat gluten; corn gluten meal was chosen as a standard to track the difference between the two sources of gluten. The response to the protease digestion was at near completion signifying that the protease worked equally well. However, the optimal conditions are in stark contrast to those for wheat gluten and the other feedstocks (72°C,pH7.5,0.75%w/w,<4hours[20]). Lower temperatures and more discernible lower loadings have a major positive impact of the degree of protein solubility. For example, at 50°C, 120hours the difference between 1.0%w/w and 0.1%w/w is well over 50%. Residence time also plays a significant role with 120hours clearly more advantageous than 24hours. On the other hand the proportion of small peptides is 75 – 80% for lower loadings and in the range of 95% for higher loadings.

Genencor listed a large range of working conditions and it is clear from the experiments that the optimal conditions are very feedstock dependent. Yet these optimal conditions are only expressed in terms of protein solubilisation yield, the relation to energy demand at those conditions must also be taken into account to grasp the full picture.

5.4   Calculations

5.4.1   Bioprocessing Energy Costs

5.4.1.1   Pretreatment/Ethanol Processing Costs
The chosen conditions for the particular feedstocks were modelled in the AFEX quench recovery Aspen+ simulation model supplied by Dartmouth University[14]. Listed in the table (see Table 7) are the direct and cumulative energy demand (CED) of the pretreatment and recovery system in relation to the quantity of ethanol produced following the conversion rates mentioned in the next section.

Table 7   AFEX Pretreatment Energy Costs

| Feedstock | Direct Cost | Cumulative Cost | Function of Ethanol |
| | Energy | | CED |
	GJ/ton ethanol		GJ/GJ/tonEtOH (%)
Stover	2.12	2.71	10.1
Wet Cake	1.91	2.40	9.3
Wet Cake + Stover	1.97	2.51	9.0
DDGS	2.00	2.55	9.5
Gluten Meal	1.88	2.37	8.8

Direct energy is the net energy used in the process while the cumulative energy takes into account the inefficiencies, different types and sources of energy for the propagation of the direct process energy, i.e. the gross energy input. The difference in direct and cumulative energy already indicates a further energy reduction possibility of around 12% by employing a better integrated source of heat. A considerable difference is present between the various ethanol production routes in terms of energy. Dry grind and wet milling, though economically inexpensive, both have high energy demands. Per ton of ethanol produced a dry grind costs 17.23 and a wet mill 19.16GJ of total coal equivalent[21]. The state-of-the-art cellulose to ethanol (corn stover) plant using dilute acid and a combined heat and power unit is considerably lower at 9.51GJ/ton[19]. In the pretreatment stage alone it has been calculated that 1.75GJ/ton energy are required. This is lower than the AFEX demands as shown in Table 7, however the biomass-to-ethanol conversion rates must also be taken into consideration. For the dilute acid process yields are 77.4% and 72.0% C6 and C5 carbohydrates to ethanol, respectively. Those for AFEX are higher at 74.0 – 94.1% as mentioned for each of the investigated feedstock in the results sections.

5.4.1.2   Protease Costs

Specific data behind the production methods of enzymes is for the large part confidential. The industry is very careful about divulging specific information regarding their formulations. The exact energetic production costs of Protex 14L are thus unknown and must be based on generalizations. Yet, these can be made as the major direct and indirect energy costs are associated with the glucose source, maintaining the fermentation heat, electric stirring and nutrient supply. A detailed master thesis was prepared using recent Novozymes A/S production data and found a cumulative energy demand to range from 22 – 234MJ/kg for 11 formulated product enzymes[22]. Other less detailed studies have also been made and place the energy costs in a similar range. When referring in general terms, Novozymes A/S uses 43GJ/ton formulated enzyme product as the total energy costs of enzymes and will be incorporated in this paper.

5.4.1.3   Protein Solubilisation Costs

The range of protease conditions were simulated in Aspen$^+$ for all the feedstocks. Process heat integration was included as a means to reduce the heating costs by making a 37°C stream available after the protease reactor, presumably for fermentation heat. A modern digester is typically equipped with an insulating mantle reducing heat losses to 8% per day or 0.333% per

hourly operation interval. The values were coupled with the resulting and presumed protein solubilization yields. Considering the main objective of the study the protease operation energy costs are given for both the wet cake and the DDGS feedstocks, see Figures 3 & 4. It is clear that high temperature with short residence times, like 72°C for 6hours, are energetically intensive. Maintained at the same high temperature, the greatly increased solubility yields achieved over the long residence times, like 120hours, counterbalance the initial high energy input. For each feedstock the optimal condition can be determined by either (1) the lowest energy input per ton or (2) by additionally relating the protein solubilisation yields with the energy cost:

- Wet Cake (1): 3.40GJ/ton protein @24hours/40°C = 0.118ton protein/ton feedstock
- Wet Cake (2): 6.21GJ/ton protein @120hours/40°C = 0.175ton protein/ton feedstock
- DDGS (1): 3.42GJ/ton protein @24hours/40°C = 0.120ton protein/ton feedstock
- DDGS (2): 4.19GJ/ton protein @120hours/72°C = 0.165ton protein/ton feedstock

Even though the yields are lower than at longer residence times the greatly lower energy demand speculates the operation parameter decision.

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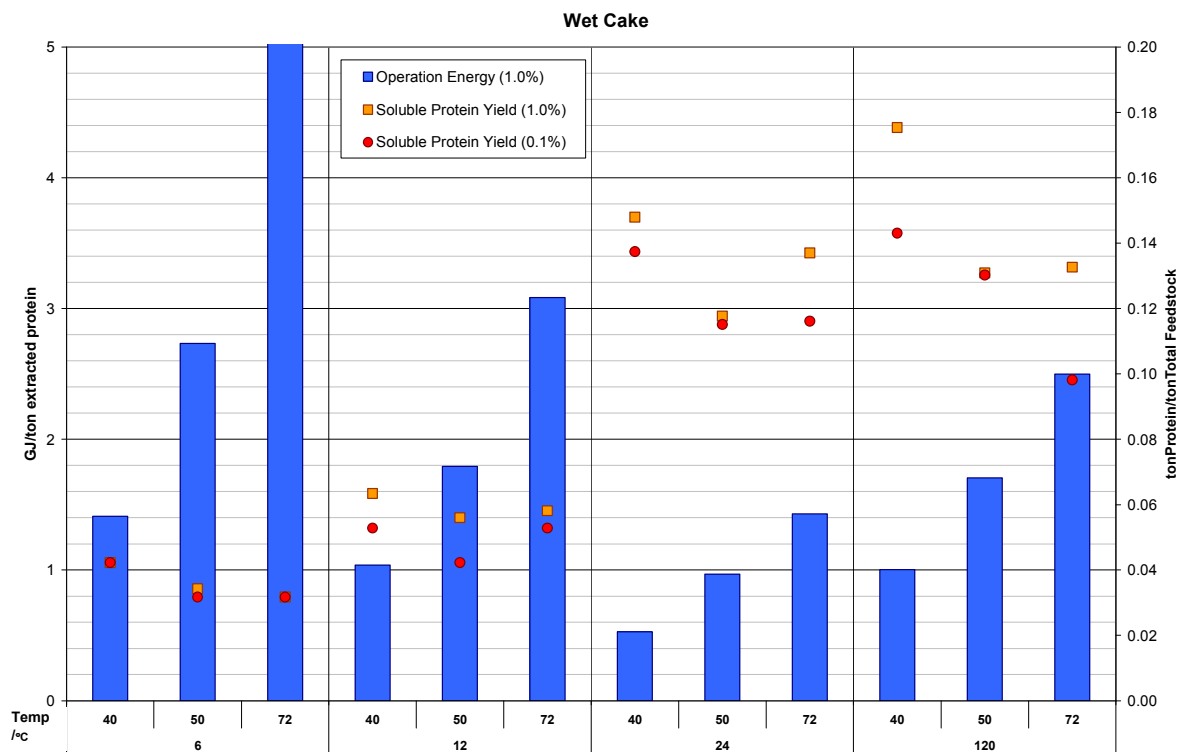
Figure 3   Wet Cake Protease Operational Costs
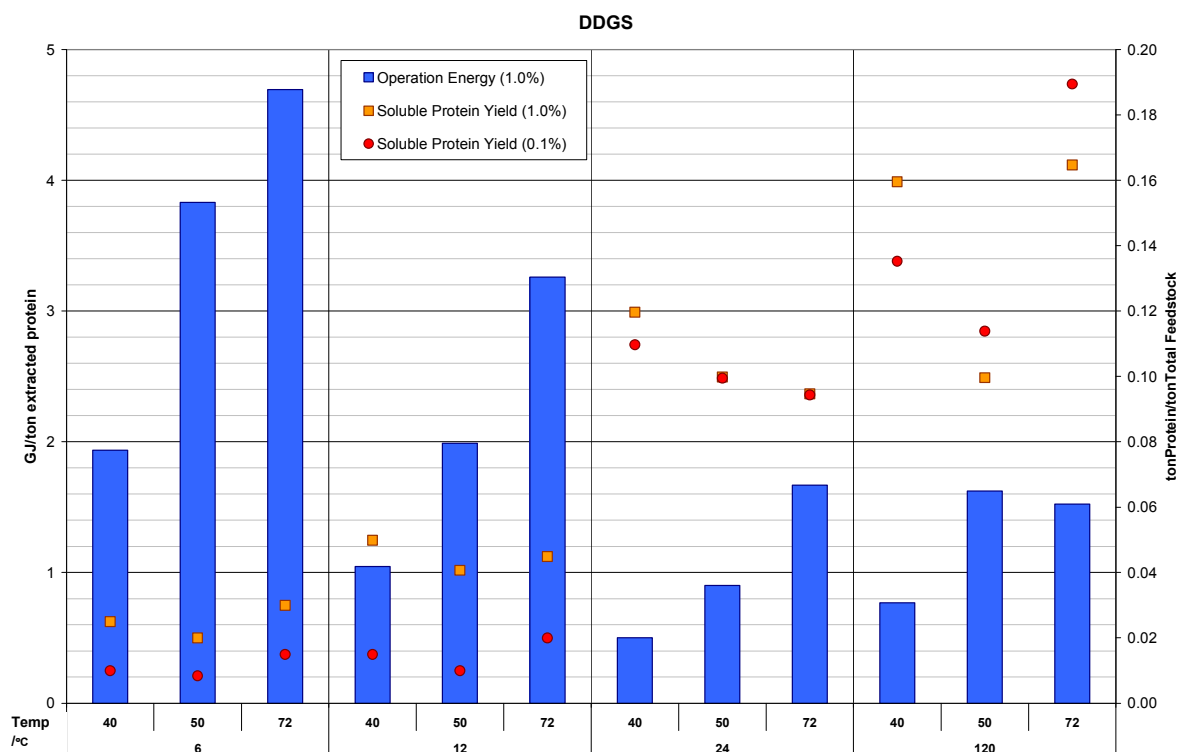
Figure 4 Dried Distillers Grains w/ Solubles Protease Operational Costs

5.4.2 *Nitrogen Containing Chemicals*

Corn protein, commonly known for its high concentration of gluten, has a particular configuration of amino acids. Using the amino acid analysis of the solubilized protein streams the actual distribution of the corn proteins after processing can be determined (see Figure 1). It is noticeable that the general trend remains consistent regardless of the originating feedstock: high levels of glutamic acid and glutamine combined at 16.4%, aspartic acid and asparagine at 9.1% and leucine at 10.4%. It is proposed that amino acids should be used as precursors to the nitrogen containing chemical industry[23, 24]. In this way the built-in functionality of the amines are able to by-pass some of the chemical industry's most energy intensive production routes, like the Haber-Bosch process. Protein separation and break-down into the free amino acids is the first step in facilitating a novel bioprocessing route. Although currently the production routes to chemicals are hypothetical and still on the fundamental experimental phase, several proposed routes present a large potential energy savings:

- Aspartic acid to acrylonitrile via decarboxylation, hydrogenation and hydrolization:
  - 1.0kg aspartic acid to 0.398kg acrylonitrile.
  - $CH_2CHCN = 67.4GJ/ton$ CED[25]
- Arginine to butanediamine and urea via hydrolization and decarboxylation:
  - 1.0kg arginine to 0.505kg putrescine and 0.354kg urea
  - $C_4H_{12}N_2 \approx 65.0GJ/ton$ CED(based on ethylene oxide)

- Serine to ethylenediamine via decarboxylation:
  - 1.0kg serine to 0.581kg ethylenediamine
  - $C_2H_8N_2$ = 46.5GJ/ton CED

The above production routes outline three hypothetical examples, whereas in a fully digested protein stream 20 amino acids are present. For subsequent calculations, we assume that amino acids have the potential to replace nitrogen containing chemical precursors and that the yields are 0.5kg N-chems (at 65GJ/ton CED) and 0.25kgAmmonia (at 28.4GJ/ton CED[10]) per kg amino acid. The technology behind bioprocessing, as in a biorefinery, relies on mild operation conditions and generally implies low associated energy costs. To separate the amino acids, perform the necessary reactions and isolate the final products will also take an additional energy input. The demand is expected to be relatively low and is assumed here to require an additional 2.5GJ/ton to obtain a final product.

5.4.3   Combined Heat and Power Unit

All proposed 2nd generation ethanol plants are planned to include a combined heat and power unit to supply the necessary heat and electricity to cover the operational energy demands of the entire process[19]. The residual waste streams, which mainly comprise of lignin and protein, are to be dried and combusted. This stream has a calorific value of roughly 17.5GJ/ton energy. In the simulated state-of-the-art lignocellulose designs more electricity is produced than needed in the process and tapped into the electric grid at market price. The efficiency of a new CHP unit is 85% in terms of energy[26]. In this proposed layout the residual solids from the proteases treatment (still containing large quantities of lignin) are also to be dried and subjected to combustion. A large part of the operational energy demand is covered.

5.4.4   Total Bioprocessing Energy Cost

By bringing all the data and calculations together the potential biorefinery concept can be determined for the feedstocks. Figure 5 illustrates the ethanol yield, solubilized protein yield, bioprocessing energy cost, CHP output energy from the residual streams and the net yielded bioenergy for the DDGS and WC. Although both feedstocks produce more energy than is needed to operate the system, there are some vital differences between the two feedstock performances. More ethanol is produced by DDGS feedstock whereas more solubilized protein and net energy is yielded by the WC. Proteins used as chemical precursors have the potential to become a highly value added product and can mitigate more fossil fuel energy demand per kg produced than ethanol can. Although in absolute terms, the total fossil fuel energy displaced by ethanol in the transportation sector is several magnitudes larger than the potentially protein-based nitrogen containing chemical sector. In the immediate future the main product and focal point of investigation and improvement options for the existing industry will certainly remain ethanol, siding for DDGS over WC. But when brought into perspective of overall energetics and maximum fossil fuel energy savings per ethanol facility WC does become the more attractive option.

Biorefinery System
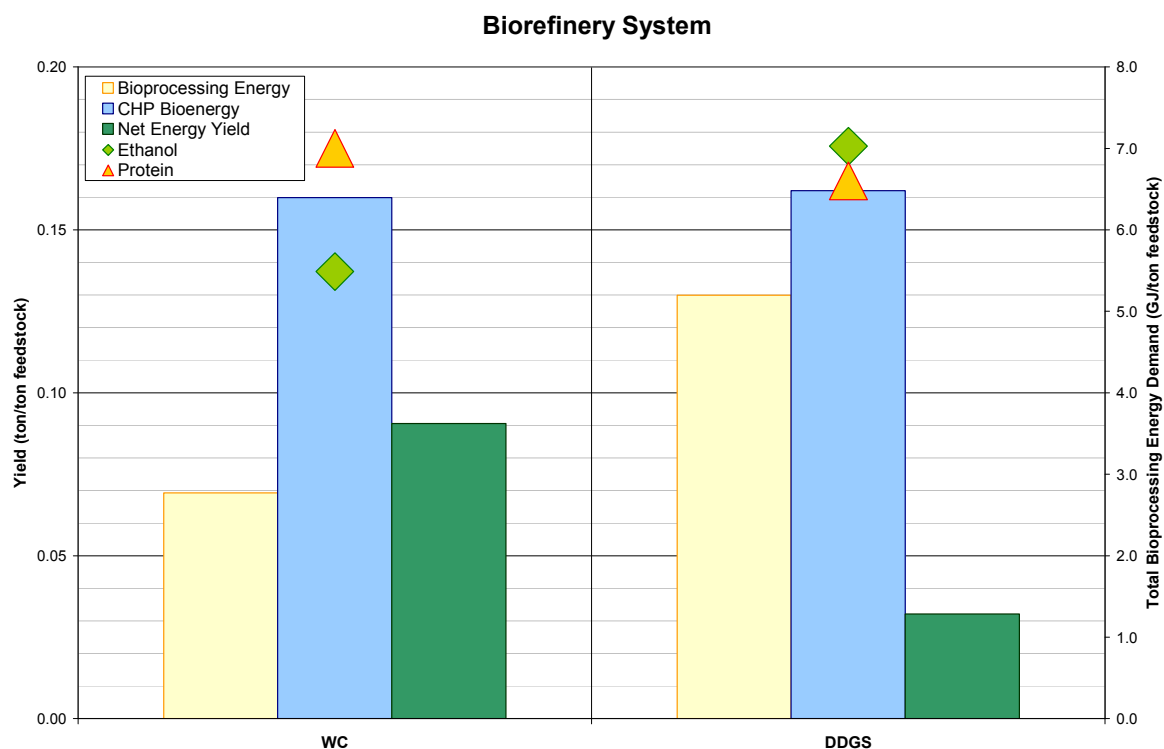
Figure 5   Biorefinery System Overview: DDGS/WC Yield and Energetics

5.5   Results and Discussion

In 2005, 14.6Mton of ethanol and over 10.0Mton of distiller grains was produced in the USA. Exposing the distiller grains to AFEX pretreatment for subsequent ethanol production can help contribute to a higher amount of total ethanol production. 1.76 and 1.37Mton extra ethanol can be potentially achieved by using the DDGS and WC feedstock respectively, which corresponds to an overall production increase of 12.1 and 9.4%. By 2012 the distiller grains market will expand approaching 14Mton that can be converted into an extra 2.46 and 1.92Mton ethanol production. Additionally subjecting the distillers grains to protease digestion can yield high quantities of soluble proteins/amino acids; DDGS: 1.66Mton, WC: 1.76Mton. Taking one of the 20 amino acids as an example, aspartic acid (9.1%) can be used as a precursor to produce acrylonitrile at a ratio of 0.398kg/kg. Acrylonitrile is a stable bulk commodity as can be seen by the high consistent production volumes; 5.24Mton in the 2005 US market. Using distiller grains as a feedstock source could potentially provide 1.14 – 1.21% of the total market share. A single percent may seem low, but consider that the current ethanol industry also only displaces about 3% of the domestic non-diesel transportation fuel market. And as that market share raises an ever increasing portion of the nitrogen-based chemical industry could be displaced by using the protein content of distillers grains as precursors. Aspartic acid is one of twenty; each of the amino acids could be used for an individual or common functionalized chemical commodity alluding at a huge market potential. Arginine as a potential source for butanediamine production perfectly illustrates this statement, for even at the low protein concentration of 4.6% and

stoichiometric ratio of 0.505kg/kg, the entire current global production of 0.17Mton could be replaced by distillers grains.

As the ethanol industry transitions to include lignocellulosic feedstocks, the distiller grains will certainly be a good candidate during the initial implementation phases. Corn is a traditional and highly desirable bioenergy crop in America and 2nd generation technology (like AFEX) will allow for a larger degree of the harvested crop to be used as a feedstock, namely stover. Stover and distiller grains can be mixed together based on their agricultural and crop yield ratios and subjected to the same AFEX/protease procedures. This paper has outlined that already on the lab-scale the system is possible with all feedstocks and would yield significant volumes of ethanol and protein at low energy costs. On the field slightly more stover material is produced than the corn cob, at 10.9ton/ha and should all the 6.87Mha of land currently needed to satisfy the corn-ethanol plants include stover an additional feedstock volume of 74.9Mton would be available. Following the results of the AFEX/protease system an extra 22.82Mton of ethanol and 1.73Mton of protein could be produced with a net processing energy gain of 9.2GJ/ton feedstock.

5.6   Conclusion

The current ethanol industry based on the starch content of corn grains is faced with the dilemma of increasingly large production volumes of distiller grains sold in a co-product market that is becoming saturated and devaluated. At over 30% protein, the material is high in protein content which if isolated can be used for other higher value added products, such as bulk chemical precursors. Similar quantities of fermentable lignocellulosic material are also present which can be used for additional ethanol production. AFEX coupled with protease (Protex 14L) digestion can liberate high quantities of fermentable sugars and can solubilise a large proportion of the protein content. Protease digestion is a feasible option to separate a good portion of the protein content of the distillers grains at a relatively low energy cost. Existing production facilities can expand to incorporate these modern methods and as biotechnology continues to develop even other high added value co-products are imaginable. With each expansion and improvement option a larger portion of the harvestable crop can be used and will result in an overall better energetic system promoting the goals of sustainability. Combining dry grind with AFEX pretreatment for stover and wet cake ethanol production with protein separation for chemical use is one foreseeable option to create a mature and more sustainable ethanol industry.

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Protein separation using protease digestion from wheat stillage
within a dry grind ethanol facility

6

Abstract

As the current starch based ethanol market increases at its rapid pace, finding new markets for the primary co-product, distiller's grains, has gained considerable interest. One possibility is to isolate the protein-rich fraction for use as precursors to biochemicals and bioplastics, further decreasing fossil fuel consumption. This research focuses on enzymatic extraction of protein peptides from wheat heavy stillage using commercially available proteases. The energy saved due to this process ranged from approximately 1.5 to 3.0 GJ/ton wheat stillage. Using Protex 6L (Genencor), approximately 57% of the protein in the stillage was soluble 24 hours after protease addition at 0.1% w/w loading. Of these proteins, approximately 32% were already soluble, indicating the importance of using heavy stillage (wet) as the feedstock rather than dried distiller's grains. Peptide size was less than 6 kDa. Further improvements in protein removal may be obtained through a fed batch addition of protease as well as improved protease cocktails.

Keywords

Wheat, Ethanol, Protein, Protease, Distiller's grain

6.1 Introduction

In recent years, the European Union has shown great interest in decreasing its consumption of fossil fuels in the transportation sector. Transportation was the fastest growing energy sector in Europe during the 1990s, with petrol and diesel oil accounting for 38% of the energy mix in 2000[1]. Reducing oil use would help satisfy the limitations imposed on carbon emissions from the Kyoto Protocol, while also reduce dependence on politically unstable regions causing fluctuating market prices and disrupting oil supply[2]. Transportation fuels from biomass, such as biodiesel and bioethanol, are seen as a near-term solution to reducing carbon emissions, as they can be easily integrated into the existing infrastructure. Gasoline demand, which accounts for roughly 40% of the main liquid fuels in transportation, is expected to increase from 130 million tons of oil equivalent (Mtoe) in 2000 to 145 Mtoe by 2020 in the EU-25 countries, indicating a great potential for bioethanol use to offset this demand. As such, a variety of directives have been proposed by European governments to increase biofuel market share. For example, in 2003, the European Union suggested that member states should have 5.75% of its transportation fuel to come from biomass by 2010[1].

Due to these incentives, converting starch and sugars into ethanol has seen a rapid growth, with European production growing by 71% to 1.56 billion liters in the past year[3]. Much of the starch-based processes use the dry grind technology, in which the grain, primarily wheat in Europe, is liquefied and the starch fermented into ethanol. After the ethanol is removed, the remaining heavy stillage is centrifuged to produce a wet cake consisting of the insoluble portions of the grain as well as thin stillage, which contains the soluble portions. Often, both portions are dried and combined to produce distiller's dry grain and solubles (DDGS), which is then sold as an animal feed.

The use of DDGS as a coproduct is deemed necessary due to the high costs, both economic and energetic, of producing ethanol from corn or wheat. By investing the energy necessary to dry the unfermented residue, the producers are able to recover the valuable protein portion of the biomass. However, there are several problems with this approach. Drying the distiller's grains is a costly process, requiring for corn approximately 2.5 GJ/ton dry distiller's grains[4]. Furthermore, both wheat and corn DGS is deficient in lysine, the limiting amino acid in nonruminant diets, which along with its high fibre content make it a poor protein source for nonruminants, and can only be added in limited quantities in their diets. In addition, the digestibility of key amino acids in DDGS is lower than in untreated grains, further lowering its value as a feed source[5].

Thus, attempts have been made to increase the value of the unfermentable residue of ethanol processing. The production of ethanol from the remaining fibre has gained significant interest, as it provides value for the producer while simultaneously further reducing the dependency on oil[6]. However, even in this case the value of the proteins in the product cannot be ignored. The remaining solids will have an increased protein content[7, 8], but their value as animal feed may still

be limited due to high oil or low lysine content[9]. Previous attempts to isolate the proteins, whether in aggregate or specific proteins, have often met with low yields[10]. For example, Wolf et al. was unable to achieve yields of zein higher than 10%[11].

An alternative approach is to use proteases to break down the proteins into smaller peptides or component amino acids, thereby increasing their solubility. This approach also opens up the possibility of using individual amino acids as feedstocks for industrial downstream processing. Several chemicals currently produced in the petrochemical industry can also be produced using various amino acids as the starting material[12]. Such methods can greatly increase the value of the protein while further reducing the use of fossil fuels. Initial studies to remove protein from corn wet distiller's grains after enzymatic hydrolysis of the fiber fraction released approximately 130g protein per kg feedstock, indicating the promise of this approach[4].

However, very little work has been done on separating the protein and fiber components of wheat DDGS. In addition, there have been no attempts to isolate protein from the stillage prior to centrifugation. The aim of this paper, then, is to investigate the possibility of removing and hydrolyzing protein from wheat stillage using commercially available proteases. Of primary importance is improving the yield of soluble peptides and amino acids while simultaneously keeping production costs and energy intensity low.

6.2 Materials and Methods

The feedstock used for this paper is wheat heavy stillage, obtained from Wheyfeed Ltd. (Nottingham, UK). This stillage contains the residue, both solid and soluble, in a dry grind process immediately after distilling off the ethanol. The dry weight of the stillage was 14.4% of the total weight, with the insoluble portion of the stillage at 10.4% of the total weight while the solubles contributed 4%. Nitrogen analysis gave a total protein content of 37.8 mg protein per g stillage (270 mg protein per g dry weight). The pH of the stillage was 3.5. Three commercial protease or protease cocktails were tested. Most experiments used Protex 14L (Genencor), obtained from *Bacillus thermoproteolyticus*, due to its use in breaking down wheat gluten, which was deemed the most similar feedstock to these experiments. Protex 6L (Genencor), obtained from *Bacillus licheniformis*, a protease most active in alkaline solutions, and Protex 51P (Genencor), a cocktail of endo and exo peptidases from *Aspergillus oryzae*, were also used.

All protease extractions and hydrolyses were performed in 50mL Erlenmeyer flasks placed in a shake-flask water bath set at 90 rotations per minute. Unless otherwise stated, the temperature was held constant at 50°C. An amount of stillage equal to 2.0g dry weight was added, and the pH brought up to 7.5 by the addition of 3.6mL of 1.0M NaOH. Water was added to bring the mixture to 20g total weight. Although higher concentrations may be used in industry to decrease energy use downstream, this 10% solid loading was deemed to be an acceptably high solid loading while remaining easy to handle and remove samples. Protease was added based on weight, as the operational energy costs in the model were based on weight rather than activity.

Unless otherwise stated, protease was added at 0.1% w/w loading, or 1g protease per kg stillage protein. Samples for analysis were taken at 24 hours after the addition of protease.

The protease was added in a fed-batch mode in certain treatments. Total protease loading was set at either 0.1% or 0.2% (w/w). Protease was added in one, two, or three equal amounts, with 24h residence time in between each addition. Samples were taken after 24, 48, and 72 hour residence time, with residence time beginning at the addition of the first batch of protease.

In certain treatments, the stillage was allowed to incubate for one hour at 70°C prior to the addition of protease in an attempt to extract extra proteins from the insoluble matrix. The stillage was brought to the desired pH to either 7.5 or 12 using 1.0M NaOH and placed in a shake flask incubator. After 1h, the flasks were cooled and the alkaline flasks neutralized with HCl prior to the addition of the protease. Residence time was measured as beginning from the time of protease addition. Samples were then taken immediately after neutralization as well as 24h after protease addition.

The primary method of protein quantification used was by amino acid analysis. All peptides that were solubilized were assumed to be available for bioplastic precursors. Samples were centrifuged at 13000 RPM for five minutes in order to remove suspended solids, and the liquid portion hydrolyzed into individual amino acids by heating at 110°C in 6M HCl overnight. The acid was removed by evaporating under a vacuum at room temperature and the samples resolubilized in 0.1N HCl. The amino acids were then derivatized using 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate (AQC) and separated using a Waters Nova-Pak c18 amino acid column. The amino acid peaks were measured and summed together to obtain the total protein. Tryptophan are destroyed during acid hydrolysis, while serine was not properly quantified by the HPLC. Furthermore, methionine and cysteine are converted to methionine sulfone and cystic acid, and thus also not detected. Thus, the protein value obtained was adjusted upward using an amino acid profile averaged from multiple milling companies to estimate the added weight of the undetected amino acids. The weight of the protease added was then subtracted from the final amount of protein, as it was assumed that all of the protease added would be present in the liquid phase.

In addition, the effectiveness of protease digestion was estimated using gel electrophoresis. Approximately 5uL of samples were loaded on Invitrogen (Carlsbad, CA) 10% Bis-Tris precast gels with MES SDS running buffer. The lower size limit of the gels was 6 kDa.

A detailed description of the methodology used to determine the operational energy required for the protease digestion conditions can be found in previous work with corn distiller's grains[4]. The model assumes an integrated peptide recovery process in addition to lime pretreatment and subsequent hydrolysis and fermentation of the fiber fraction of the biomass. This same Aspen+

calculation model with energy integration considerations was used for the wheat feedstock. Internal operation energy is thus calculated by combining the cumulative process energy (CED), total direct and indirect fossil energy costs associated with protease production, and the process energies (Aspen model). As the solubilized amino acids are proposed to be used as precursors to the chemical industry, the energy savings potential is determined by comparing the CED of the traditional petrochemical production route with the resulting CED of the amino acids to equal chemicals[4, 12].

6.3   Results and Discussion

Increased temperatures appear to improve protein solubility up through 60°C, but solubility decreases at 70°C, as seen in Figure 1. There was a greater proportion of large proteins in the 70°C samples compared to 50°C and 60°C after a 24 residence time, suggesting that protease activity significantly decreases at higher temperatures (data not shown). This is consistent with previous studies with corn DGS, although inconsistent with the manufacturer's stated tolerance of 72°C (Brehmer 2008). However, despite the lower activity, a significant amount of protein was liberated. Thus, the temperature likely has an effect outside of protease activity. Higher temperatures can open up the structure of proteins, breaking covalent bonds between different proteins, thus freeing them. For all future experiments, the temperature was set at 50°C for protease digestion, as there was no appreciable difference in protein solubility between 50 and 60°C while the energy consumption is 0.75 GJ/ton lower at 50°C compared with 60°C, due primarily to the costs required to heat the stream from 20°C to the desired temperature.
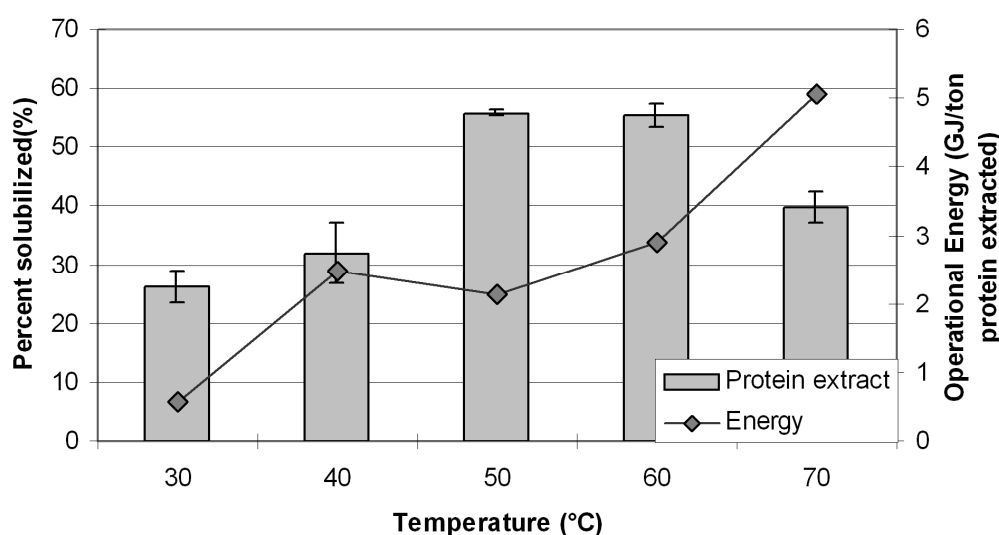
Figure 1   The Effect of Temperature on Protein Solubilized.
- Data is for 24 hours of protease digestion at 1% w/w loading of Protex 14L.
- Extractions were performed at a pH of 7.5 and 90rpm.
- Bars represent the amount of protein in solution relative to the total protein present, while the diamond connected line represent the operational energy in relation to the solubilized protein.

Figure 2 shows the rate of protein solubility for both high (1.0%) and low (0.1%) protease loadings up through 168 hours of protein digestion. Low protease loading approximately

doubled the amount of protein in solution after 24 hours, but very little additional protein was released after this point. Higher protease loadings showed both an improved rate and extent of protein solubility, continuing to release protein throughout the experiment. The reduced rate of protein solubility is likely due to protease degradation over time, either due to protein unfolding or the protease attacking itself. Gel electrophoresis suggests the latter explanation, as no band is seen for the protease after 24 hours (data not shown). Approximately 18% of the total protein is available as soluble protein prior to protease addition, demonstrating the importance of using whole stillage as the substrate rather than solely the insoluble material. Furthermore, more protein is initially soluble in the stillage for wheat compared to corn (Wilkie 2000), indicating that wheat based dry mills may be better suited to this technology than corn.

6
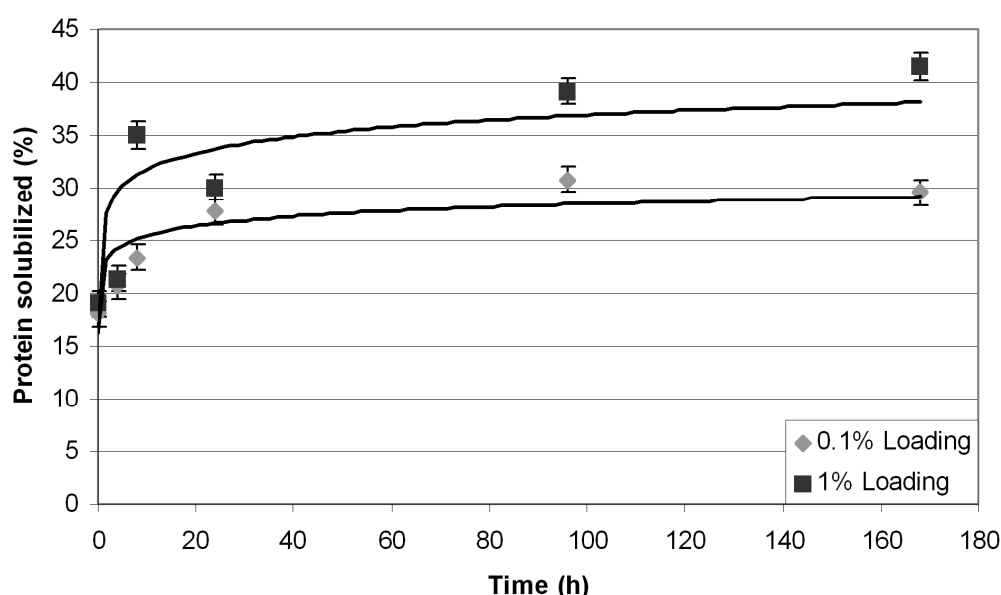
Figure 2   Protein Removal Rate During Protease Digestion
- Both low (0.1% w/w) and high (1.0% w/w) loading of protease, lines represent best logarithmic fit.
- Amount at 0h represents the initial soluble protein within the whole stillage.
- Extractions were performed at 50°C, a pH of 7.5, and 90rpm.

For all time periods and both solid loadings, the energy used in this process is less than the conventional fossil fuel route for chemicals, as seen in Figure 3. Due to the increased amount of protein solubilized, the operational energy cost per ton of protein solubilized is less for 1.0% protease loading than for 0.1% loading at all time periods. Here, the overall energetic savings are highest at 168 hours of digestion and high protease addition, with over 3GJ/ton stillage saved in comparison with petroleum based plastics. For both low and high protease loading, energetic savings tend to increase as residence time increases, indicating that the energetic costs of maintaining the digestion is slight compared with the additional protein yield. While the higher protease loading sees greater yield and therefore energy savings, the high cost of these proteases (upwards of 200€/kg) may make such high loadings unfeasible in the marketplace.
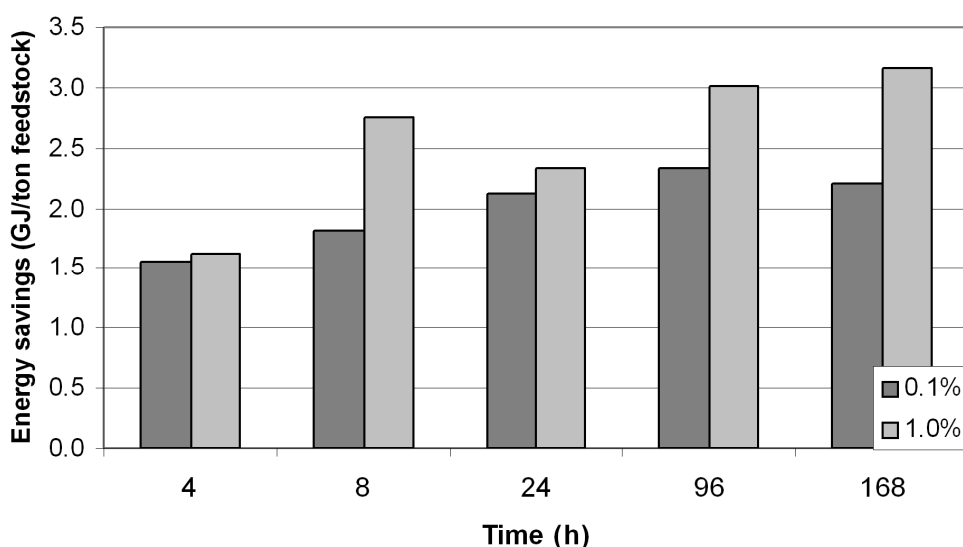
Figure 3   Total Potential Energy Savings
   - Both 0.1% and 1.0% (w/w) loadings at multiple time periods of digestion when compared to conventional fossil fuel production routes.
   - Feedstock refers to the original agricultural portion prior to processing.

Thus, it seems appropriate to focus primarily on improving the digestibility at low enzyme loadings. Various approaches were considered in order to increase the effectiveness of protein digestion based on the information above. If the protease is indeed breaking down over time, then a fed-batch approach to protease loading could improve its effectiveness. In addition, grain proteins are often susceptible to alkaline solid/liquid extraction, particularly at high temperatures, thus suggesting that an extraction prior to protease addition may improve yields[13, 14].

The results of the fed-batch experiment can be seen in Figure 4. Samples with initial protease loadings below 0.1% did not perform as well at 24 hours, suggesting that further decreases in protease loading may not be an effective solution. However, additional loadings at 24 and 48 hours did improve protein digestion, bringing lower loadings equal to the initial 0.1% loading. As expected, no additional improvements in yield were seen at later time periods in the control. No significant differences were seen between an initial 0.2% loading and two separate 0.1% loadings. Thus, any possible improvement in protein digestion due to fed-batch protease loadings is inconclusive. A complete study to fully optimize protease loading and fed-batch addition would be needed to determine if such a scenario could increase protein yields further.

Attempts to extract the proteins prior to protease addition are seen in Figure 5. The high temperatures used were necessary to obtain a significant extract. As expected, the initial amount of protein in solution increased when a prior extraction was performed, although little difference is seen between the neutral and basic extracts. This led to a subsequent increase in the final protein concentration in solution after protease addition. Despite the increase in protein concentration, virtually all of it is still broken down into smaller peptides (data not shown). Thus,

it is likely that the number of active sites within the insoluble matrix is the limiting factor in the release and breakdown of the proteins, rather than the activity of the proteases themselves.
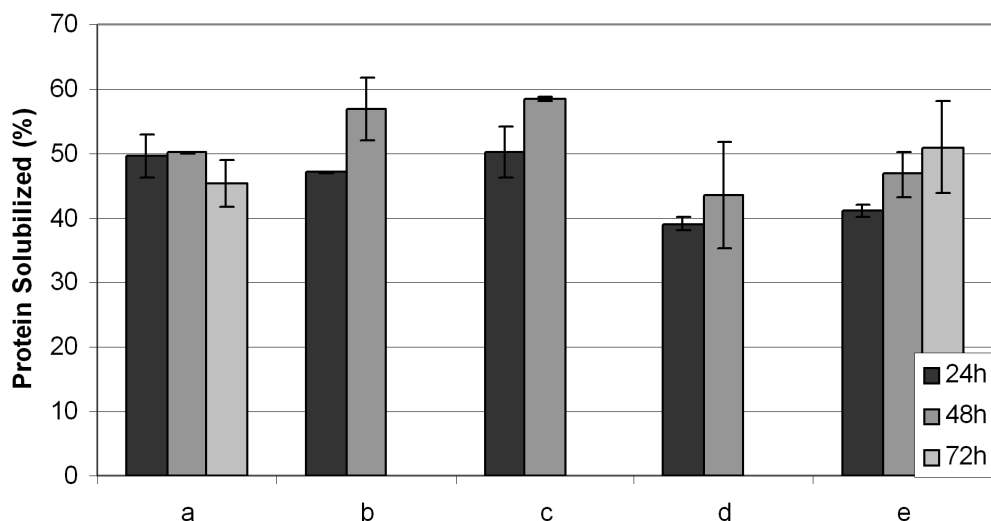
Figure 4   Effect of Fed Batch Addition of Protease on Protein Solubility
- a) 0.1% (w/w) protease addition at 0h, b) 0.2% protease loading at 0h, c) 0.1% loading at both 0h and 24h, d) 0.05% loading at 0h and 24h, e) 0.033% loading at 0h, 24h, and 48h.
- Digestions were performed at 50°C, pH 7.5, and 90rpm.
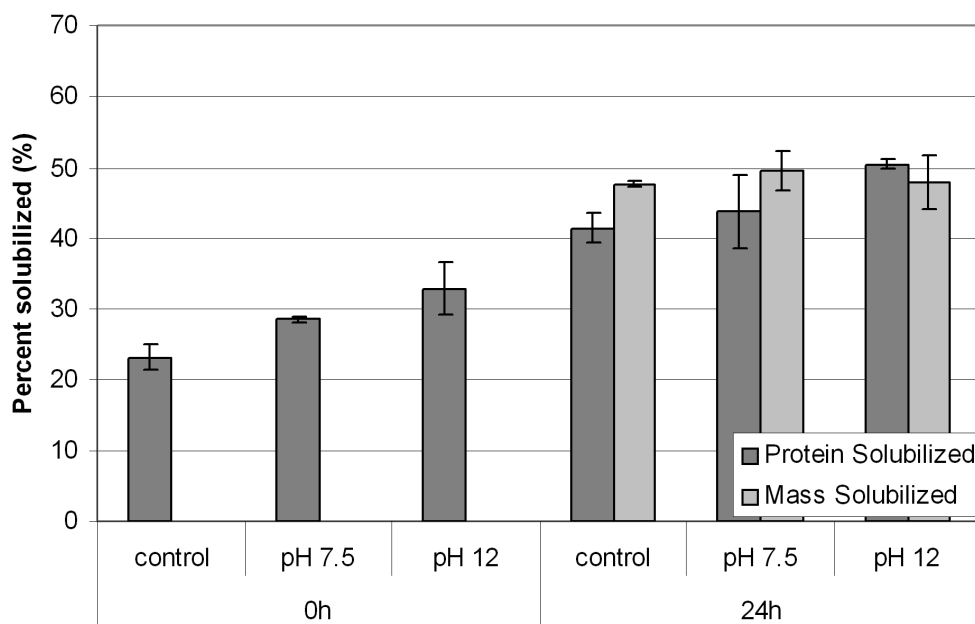
Figure 5   Effect of Extractions Prior to Protease Addition
- Control is protease digestion without extraction.
- Extractions were performed at two different pH levels at 70°C for 1h.
- The alkaline extract was neutralized prior to protease addition.
- Time at 0h represents the beginning of protease digestion.

116

It is interesting to note that, despite the lack of initial increase in protein removal in alkaline extraction, the final result after the addition of proteases did continue to increase the protein removal. Thus, the alkaline conditions may also be opening up more sites for the protease to attack.

Due to the slight improvement seen with alkaline extraction, the alkaline protease Protex 6L was also tested. In addition, Protex 51P was tested due to its exopeptidase activity, as well as a combination of 51P and 14L. Protex 6L digestions were performed at pH 10, the optimal level suggested by the manufacturer, whereas 14L and 51P digestions were performed at pH 7.5. As seen in Figure 6, Protex 6L showed a significant improvement over the other two proteases. This could be due to the increased solubility at alkaline conditions. The exopeptidase enzymes released fewer proteins than either of the other two enzymes tested. This is most likely due to a decrease in active sites, as the ends of the proteins are embedded within the insoluble matrix or have been modified during the original dry grind process. The combination of 14L and 51P was only slightly lower than 14L alone, despite the decrease in 14L loading. This indicates that there may be some synergistic activity between the two types of protease, indicating other protein combinations may also improve protein removal with lower overall loadings.
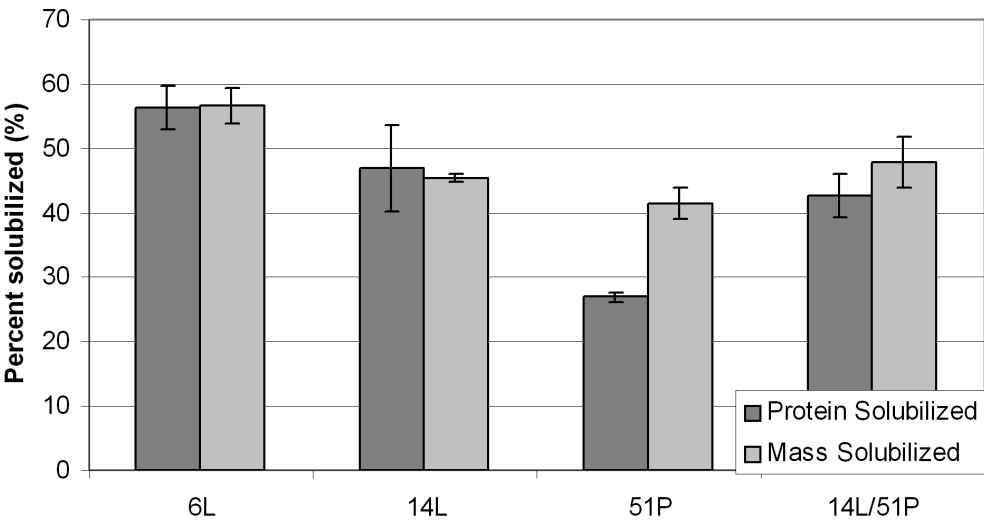
Figure 6   Effect of Different Proteases on Protein Removal.
- Enzymes used are Protex 6L, Protex 14L, and Protex 51P.
- Digestions were performed for 24h at 50°C and 90rpm.
- Protease was loaded at 0.1% (w/w) and the pH was kept constant at 7.5 for Protex 14L and 51P and 10 for Protex 6L.

Figure 7 shows the effect of Protex 6L protease digestion on the amino acid profiles of the stillage. Both the profile of the whole stillage as well as the soluble portion are shown for comparison. In general, the protease digestion served to moderate the amino acid profile, increasing the relative ratios of amino acids that were not originally soluble in stillage. However, relative amounts of both aspartic acid/asparagine and lysine increased more than expected, while glycine and histidine decreased more than expected. Proteases attack at specific sites within a

protein, and thus are not likely to attack all proteins equally. Thus, a protease cocktail may help digest specific proteins or peptide sequences that Protex 6L alone is unable to attack, potentially increasing the yield of soluble amino acids.
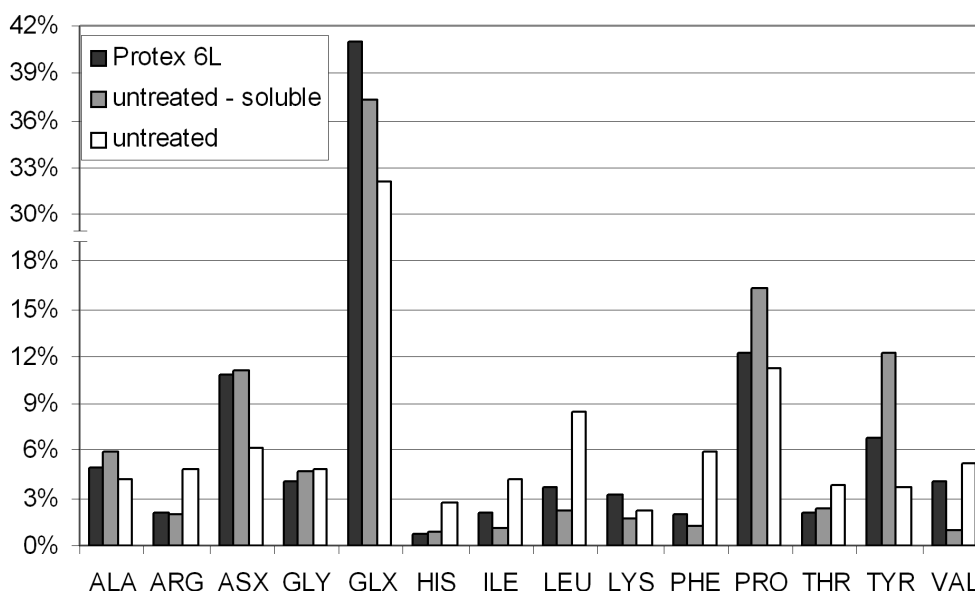
Figure 7   Amino Acid Profiles for Proteins Released by Protex 6L
   - Soluble proteins in wheat stillage, and total proteins in wheat stillage.
   - Met, Cys, and Trp were not detected due to being destroyed during acid hydrolysis.

6.4   Conclusions

Protease extraction of wheat stillage using 0.1% Protex 6L yielded a maximum of 57% of protein in soluble form. Approximately 32% of these proteins were already soluble prior to protease addition, indicating the importance of using the whole stillage as a feedstock rather than solely the solid distiller's grains. These soluble proteins as well as those extracted were effectively broken down into smaller peptides as well. With 0.1% protease loading, digestion was essentially complete after 24 hours. Improvements in protein solubilization were also seen with an alkaline extraction prior to protease addition for proteases active in neutral conditions. Increased protease addition primarily improves both the extent and rate of hydrolysis, although the high costs of enzymes may be prohibitive. Thus, rather than additional expensive proteases, lower protease loadings added in a fed-batch method may prove to be more cost effective. In addition, a cocktail of different alkaline proteases may further improve yields and therefore reduce carbon emissions.

These results indicate that protease extraction of wheat stillage is a promising option for further processing within dry grind refineries. The peptides removed may be used as precursors for bioplastics, whereas the remaining fibre in the solids can be hydrolyzed and fermented into additional ethanol. It remains to be seen if the peptides can be effectively separated from the

remaining material within solution, as well as the subsequent operations required to convert the amino acids to the desired end products.

6.5   Acknowledgements

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6

Implementing an energetic life cycle analysis of lignocellulosic
feedstocks with protein separation for the chemical industry
from the existing bioethanol industry

7

Abstract

The biofuel ethanol is currently being produced in large quantities from corn in the US and from wheat in the EU and further capacity expansion is expected. Relying on so-called 1st generation technology, only the starch contained in the edible portion of the crops (ears/grains) are subjected to fermentation. Following life cycle calculations reveals minute levels of fossil fuel replacement placing doubt on its renewability and an imbalance on the domestic animal feed markets are immerging due to the by-product distiller grains. Additional utilization of the lignocellulosic and protein components of the by-product through new developments has the potential to alleviate both setbacks. A cradle-to-factory gate analysis was performed on a variety of bioethanol production layouts incorporating the newest technological developments to determine the maximum fossil fuel reduction potential. Expanding to include lignocellulose pretreatment for ethanol production with protein separation for amine-based chemical production can increase the fossil fuel mitigation potential by seven- to ninefold for US-corn and five- to eigthfold for EU-wheat bioethanol facilities.

Keywords

LCA, Ethanol, Corn, Wheat, Protease, Energy

7.1 Introduction

The continuing pressure of soaring oil prices and growing environmental constraint is increasingly drawing attention and policy towards the development and use of biofuels [1]. In the USA, the Renewable Fuels Standard has allowed the bioethanol market to thrive with 29.86Mm³ produced in 2007[2]. Following the New Renewable Fuels Standard Schedule by 2012, it is expected that the traditional production methods will nearly double output to 50.0Mm³ of bioethanol. Between 100 and 120Mton of corn *(Zea mays L.)* ears are required to fulfil this demand, for in the near future, it will remain the primary feedstock of choice. In Europe, the current bioethanol production is trailing behind but has already reached 3.69Mm³ annual production[1, 3]. Should the newly proposed guidelines of the EC be followed the European biofuel market, including biodiesel and bioethanol, will continue to increase rapidly[4]. While the 2010 goal of mixing 5.75% biofuels into the road transportation market is certainly overly optimistic and under debate[5, 6], realistic predictions foresee an increase to 6.0Mm³ domestic production[7]. Here the feedstock tendency is towards the grains market with wheat *(Triticum aestivum)* dominating the choice. In such a situation around 17.4Mton of wheat grains (dry) will be required to achieve the predicted levels.

Following the standard 1st generation dry milling practices to produce ethanol from the starch contained in the corn and wheat feedstock, a large quantity of the by-product dry distillers grain with solubles (DDGS) is generated; 0.92ton per ton ethanol for corn and 1.73ton per ton ethanol for wheat. DDGS is both rich in proteins and fibre resulting in these large volumes being currently supplying the animal feed market as a ruminant feed substitute. Despite increased meat consumption trends both domestic feed markets are expected to become saturated as the biofuel market expands causing the forecasted market value of DDGS to fall and thus negatively affect the overall economics of ethanol production [8]. The emergence of new technologies within the renewable energy sector is presenting alternative product options for DDGS.

The buzz word within the biofuels research and development segment is "lignocellulosic pretreatment", otherwise regarded as 2nd generation technology[9]. Here the complex carbohydrates components (e.g. cellulose) are made available as an additional source for ethanol fermentation. Distillers grains contain moderate quantities of such carbohydrates (38.4% corn-derived, 40.5% wheat-derived) and can be considered as feasible 2nd generation feedstocks. Accompanying the prospect of additional ethanol production from the same quantity of original feedstock, one of the main pretences in the biofuels segment arises, the net energy discussion. *"How much fossil fuel energy is replaced?"* Second generation technologies, using the lignocellulosic components of biomass, are generally regarded as achieving a higher level of fossil fuel replacement potential[10]. Net energy value (NEV) is a useful, yet crude method to determine this amount by relating the renewable energy output to the total amount of non-renewable energy input[11]. For both corn-to-ethanol and wheat-to-ethanol systems, following the 1st generation technology, the NEV is low[12, 13]. Using the DDGS by-product as an animal feed does slightly increase the NEV, and the newer

2nd generation options should increase the value even further, yet there are other production routes for the by-product that could lead to significantly higher fossil fuel replacement potentials.

Distiller grains are marketed as an animal feed, largely in part due to their high protein content. These same proteins that can be the source of new lucrative energy saving options. Isolated and digested to their amino acid building blocks, proteins can be used as chemical precursors [14]. Basing emerging biotechnology and standard chemistry techniques on the existing chemical functionality of the amino acids has the potential to save vast amount of fossil fuel energy within the petrochemical industry[15, 16]. The first step in acting towards this biorefinery concept is separating the proteins/amino acids from the feedstock. Preliminary protease digestion experiments have revealed that 51.7% of the amino acids from corn-distillers grains can be solubilized and separated and 41.5% from wheat-distillers grains[8, 17]. These new production routes must be properly assessed for the fossil fuel replacement potential and compared systematically with the other product options from the bioethanol by-products using the same methodology. Government policies in the field of renewable energy, like the biofuels sector, are created under the pretence that all technologies are equally contributing to fossil fuel savings and subsequently sustainability; they are not. Investigating alternative production options for the existing bioethanol by-product distillers grains in light of energetics can help to guide future policies and research directions within the sector. Furthermore, by studying the corn-to-ethanol and wheat-to-ethanol process both the similarities and differences between the American and European system can be compared under the same pretext.

7.2   Materials & Methodology

The full details of this particular life cycle assessment (LCA) approach is found in one of the authors' previous articles[16]. The standard methodology of the ISO14040 series has been followed to a great extent with the exception that only the major material streams were incorporated to document the energy values as no environmental considerations were made. This is done because only the resulting cumulative process energy in terms of fossil fuels are of interest in the analysis. Furthermore, the "cradle" is set at the point of fossil fuel production as both the existing petrochemical and proposed biochemical production routes rely on a clean feed of fossil fuels. As the bioenergy, biofuels and biochemicals will be used as a replacement for existing industries and infrastructure there is a common point of cohesion. The grave, here, is set at the so-called "factory gate" where all processes, emissions and eventual disposal are identical from that point onwards. It is set at a selection of specific chemical products handled herein and at the lower heating value for gasoline and ethanol. Essentially, a "limited comparative energetic cradle-to-factory gate assessment" is conducted to determine the entire cumulative fossil fuel energy in the production of bioethanol with the various co-production utilization options.

7.2.1   Goal and Scope

Widely accepted LCA programs such as SimaPro and GaBi were not used as their abilities within the biobased economy are currently limited, thus each of the input categories is individually

assessed. A simplified material process flow diagram (PFD) leading up to and including the experimental processes is to be considered (Figure 1). Although both systems, wheat-to-ethanol and corn-to-ethanol, are different they are similar enough to use the same general scope display.
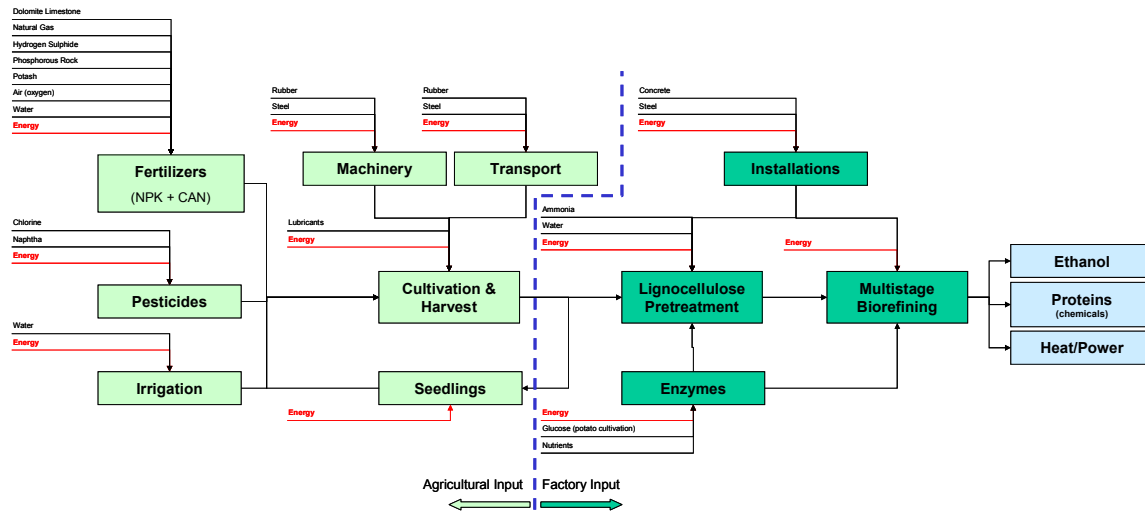

Figure 1   Simplified Material Process Diagram
- valid for both EU wheat production and US corn production

7.2.2   Data

As indicated in Figure 1 the data and calculations are separated into two distinct sections; agricultural input and factory input. All the aspects of modern agriculture are converted and expressed in fossil fuel energy terms. The data originates from a wide variety of sources and is listed as it occurs. Generally on the factory side of the assessment the best available and newest technologies are represented. Both sections also include portions of internal information and knowledge, especially in regards to the proposed bioprocessing configurations.

7.2.3   Impact Assessment

Bioenergy (like combusted biomass) and biofuels (like bioethanol) are used to offset the calorific value of the fossil-based products they displace. The calorific values and efficiencies within their intended application are taken into account to reveal their replacement potential. Biomaterials (like biopolymers) are not initially intended for combustion but to displace the associated process and feedstock energy of the petro-chemically produced material. As the grave is set at the chemical factory gate the calorific values are not suitable for these particular products options. Cumulative energy consumption (CEC) is used to indicate the total embedded fossil fuel energy (feedstock and process) of both the potential biomass-based and traditional fossil fuel-based production routes. The conceptualised biorefinery route is compared against the petrochemical route and expressed in potential fossil fuel energy savings per chemicals (or product as ethanol is included) produced (GJ/ton), per total harvested biomass feedstock (GJ/ton) and per cultivated land area (GJ/ha). Breeding factor (BF), the percentile fossil fuel energy contained in the renewable product, along side the net energy value (NEV) is also presented.

7.2.4   Feedstock Choice

Cereal grains are primary harvested for the edible portion; corn the ears (cob) and for wheat the grains (spikelet). These starch-rich biomass portions form the feedstock source currently used in the US and EU bioethanol industry. The unconverted components are collected, dewatered and end up as dried distillers grains with solubles (DDGS). Normally DDGS is dried down to a moisture content of 10 – 12.5%, with corn DDGS being 11.2%. The cost to dry wet distillers grains to these levels is intense, 2.47GJ/ton[8]. This is an acceptable final moisture content for combustion, however, a final moisture content of 0% is required to comparatively determine the optimal potential higher calorific energy output of the different distillers grains. In this case the drying energy costs are slightly elevated with the initial moisture content of corn and wheat distillers grains differing resulting in independent drying energy requirements. Drying corn wet distillers grains with solubles from 82.4% costs 3.9GJ/ton and drying wheat DDGS from 85.0% costs 4.0GJ/ton. In the previously conducted experiments[8, 18], and the calculations here within, the "wet" distillers grains will be used as a feedstock source, effectively avoiding these associated moisture reduction inputs. In addition to maximizing the utilization of the starch-rich biomass portions, the agricultural residuals will also be considered as a feedstock source. Stover (corn) and straw (wheat) are rich in complex carbohydrates and are quickly gaining interest as an independent source for 2nd generation ethanol production. Regardless, the more biomass that is used from the field, the lower the overall agricultural energy input per product output. Stover and straw are both present with a dry weight ratio of 1.25:1.0 in relation to the ears and grains portion. Figure 2 presents the chemical composition of the individual crop portions and the total overall biomass composition.

7.3   Calculations

7.3.1   Agricultural Input

The modern cultivation of foodstuffs, like corn and wheat, are highly energy intensive processes encompassing a high degree of mechanized farming. One could argue that modern agriculture is so intense that fossil fuels are indirectly converted via soil as a medium into food. Many studies, reports and governmental bodies have provided detailed information pertaining to the various stages of cultivation. Listed in Table 1 is an overview of the energy costs in relation to the different cultivation aspects for both crops in their respective region. The exact details and considerations of the calculation procedure have been covered in previous work[19]. Best practice yields and their corresponding systems have been selected, while for comparative insight average yields are also listed. The average agricultural yields, expressed in the edible portions wet weight, include all farmers in the region good and bad, large scale and small scale, industrially minded and eco-minded, etc. Realistic biomass yields included in this study pertain to the upper boundary of typical farms in the region, essentially best practice. The resulting total agricultural fossil fuel energy input is based on and related to those best practice yields including the agriculturally relevant portion and the residues.
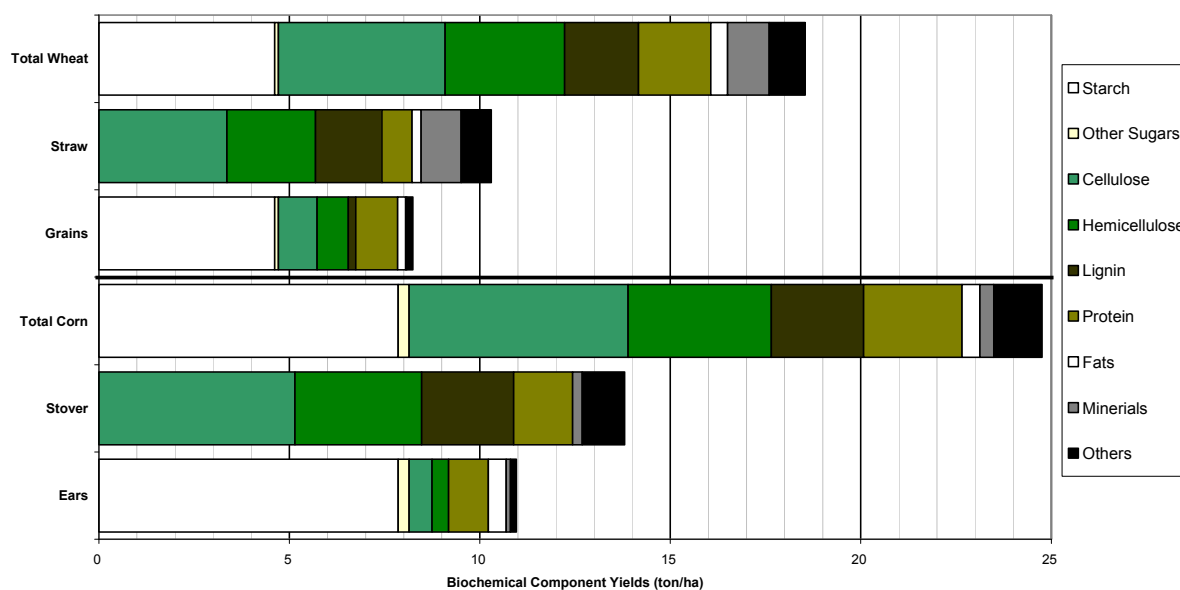
Figure 2   Biomass Composition
  - expressed in dry weight proportion

7.3.2   Factory Input

7.3.2.1   Internal Process Energy

A considerable difference is present between the various ethanol production routes and feedstock used in terms of energy. In the starch-to-ethanol production facilities the most common and recent technology currently being employed is the dry milling procedure. Based on the corn feedstock, ethanol costs 17.76GJ/ton in total cumulative fossil fuel energy[20-23]; with 1.0GJ/ton direct electric, 7.3GJ/ton direct thermal and 0.4GJ/ton from indirect sources (such as plant construction). Based on the wheat feedstock, ethanol costs slightly less cumulative energy at 15.84GJ/ton[12]; with 1.0GJ/ton direct electric, 6.3GJ/ton direct thermal and also 0.4GJ/ton from indirect sources. Corn results in an overall conversion rate of 0.480g ethanol per gram simple carbohydrate (starch) and wheat has 0.473g/g. In the lignocellulose-to-ethanol production facilities all technologies are still under investigation, whether on a laboratory scale or a pilot plant scale [9]. For the corn wet distillers grains and stover mix, as adhering to the suggestions made in the preceding article, ammonia fast fibre expansion (AFEX) will be employed[8]. The direct energy demand for ethanol is 8.25GJ/ton broken down into 7.4GJ/ton thermal and 0.8GJ/ton electric. An extra 5.66GJ/ton cumulatively from indirect sources is required (mainly chemicals and enzymes). Distinguishing between direct internal energy demand and cumulative indirect external energy demands is performed because the residue streams (lignin, etc. discussed later) is combusted and can offset the need for external energy supplies. Lime pretreatment with enzymatic hydrolysis is popular and well-studied, especially for wheat, at European research laboratories[24, 25]. The direct energy demand is noticeably higher at 12.89GJ/ton ethanol, again broken down into 11.0GJ/ton thermal and 1.9GJ/ton electric with an extra 6.97GJ/ton cumulatively from indirect sources. The overall ethanol yields for these systems and in relation to

the feedstocks differ, for the AFEX treated corn has a higher conversion rate than the lime treatment wheat feedstock. The overall corn conversion rates are 0.45g ethanol per gram complex C6 carbohydrates (i.e. cellulose) and 0.40g per gram complex C5 carbohydrates (i.e. hemicellulose). The values for wheat are lower at 0.42g per gram C6 and 0.37g per gram C5.

Table 1   Agricultural Fossil Fuel Energy Inputs

Input Category		Unit	Corn	Wheat
Area	Continent		North America	Europe
	Country/Region		Iowa	France
Yield[26-29]	Agricultural Average	ton/ha WW	9.0	7.0
	Agricultural Best Practice	ton/ha WW	13.8	10.3
	Term		Ears	Grains
	Total Yield Best Practice*	ton/ha DW	24.8	18.54
Fertilizer[19, 30, 31]	Nitrogen (N)	kg/ha**	228.6	281.9
	Phosphorous (P_2O_5)		123.9	62.9
	Potassium (K_2O)		388.2	459.8
	Lime (CaO)		5.8	46.4
	Others		151.8	71.0
	Energy	MJ/ha	1.7E+04	1.8E+04
Pesticides[32-34]	All in general	kg/ha	4.0	3.4
	Energy	MJ/ha	1.3E+03	9.3E+02
Irrigation[35-37]	Water	mm	112	175
	Energy	MJ/ha	2.3E+03	2.1E+03
Seeds[38, 39]	Rate	kg/ha	15	33
	Production Cost+	MJ/kg	4.6	13
	Energy	MJ/ha	6.9E+01	4.3E+02
Cultivation & Harvest[40-42]	Diesel	l/ha	52.08	50.52
	Labour†	h/ha	14.82	16.99
	Lubricants	l/ha	1.2	1.1
	MTR‡	%	2.5 – 16.0	
	Energy	MJ/ha	3.3E+03	3.5E+03
Sizing, Drying & Handling[43, 44]	Energyº	MJ/ha	4.4E+04	1.7E+04
Transportation[23, 45] (Regional Biorefinery)	Tractor Distance	km	10	5
	Truck Distance		15	38
	Train Distance		65	223
	Energy	MJ/ha	4.2E+03	2.3E+03
Total Agricultural Fossil Fuel Input	Energy	GJ/ha	72.2	44.3
	Energy	GJ/ton	2.9	2.3

*Total yield (best practice) includes the agricultural portion and the residues, i.e. stover, stem and leaves. Expressed in dry weight
**Linear function of best practice yields based on available yield dependent uptake rates
+Seed production energy cost is a function of the attainable seed yield and total agricultural fossil fuel input following standard procedures
†Based on machinery operation and extra field labours hours, energy input related to imbedded fossil fuel energy in the food
‡Percentage dependent on the machinery and implements used for the particular farming operation, average 7.0%
ºPreparation of feedstock for transportation and storage, including transfer operations costs

7.3.2.2   Animal Feed Co-product

Animal feed is a tricky co-product in terms of proper allocation in LCA's and due to this difficulty it has become common to leave it out all together or merely resort to the energy content. This is not the proper method when conducting a comparative cradle-to-gate analysis

for using ethanol co-products because animal feed substitutes or replaces the need of producing dedicated animal feeds. A study has published detailed information regarding the fossil fuel input to produce various animal feeds[46]. In general *"forage"* animal feeds require 1 – 3GJ/ton worth of indirect fossil fuel energy and *"concentrated"* (compound) feeds cost 6 – 14MJ/kg. Three notable compound feeds are; (1) corn gluten meal at 6.1GJ/ton with a crude protein (CP) content of 47% and a metabolic energy (ME) of 7.5GJ/ton, (2) corn grains at 9.0GJ/ton with a CP of 10% and a ME of 8.4GJ/ton, and (3) soymeal at 6.8GJ/ton with a CP of 45% and a ME of 7.9GJ/ton. In these cases, distillers grain can partly displaces locally marketed corn gluten meal, corn grains and soymeal depending on the local market conditions. The most important attributes within the compound feed industry are the metabolic energy coupled with the crude protein content. It is even common to chemically (via fermentation) produce certain amino acids (lysine, methionine, etc.) and formulate them into non-ruminant feeds. The ME of wet corn distillers grains and a typical feed mixture was compared for cattle under actual conditions[53]. The resulting values were comparable and the ME of the different compound feeds are also comparable (as listed above) meaning in this respect, the feed replacement potential will be based on the protein content relation only. For example, corn distillers grains have a protein concentration of 30.5% meaning 4.6GJ/ton fossil fuel that would have gone into soymeal production is avoided. Note that this is actually several magnitudes lower than the mistakenly allocated gross calorific value: taken drying and preparation into account, the resulting net thermal energy of DDGS combustion from the original 15.0 – 17.5GJ/ton (HHV) is 7.7GJ/ton for corn and 7.8GJ/ton for wheat.

7.3.2.3 Amine Chemistry

As earlier proposed, the proteins contained in the ethanol co-product can be used as precursors to the functionalized petrochemical industry[14-16]. In this way the built-in functionality of amines are able to by-pass some of the most energy intensive production routes in the chemical industry. The first step in the bio-based production route is separating and breaking down the proteins into their individual amino acid building blocks. Initial protease digestion experiments were performed as a proof of concept resulting in moderate solubilization rates of 51.7% for corn wet distillers grains and 41.5% for wheat stillage. The digestion process energy related to the conditions needed to achieve those solubilization rates are 6.21 and 8.17GJ/ton protein, respectively. As those experiments were an introduction to the novel concept of protease digestion to separate the amino acids, the results are sub-optimal. It can be expected that with further investigation and conditioning of the parameters a near complete digestion is foreseeable; 95% is assumed. The process energy involved will be similar but as the amino acid separation yields are increased the relative energy costs will decrease to 3.4GJ/ton and 5.9GJ/ton. After digestion the amino acids require separation, isolation and purification for further processing. A multi-step cascading process using standard techniques, based on the physiochemical characteristics of the individual amino acids, is envisioned[47]. According to a hypothetical system consisting of electrodialysis, nanofiltration, several sorts of chromatography (calculations not presented), this step requires on average 9.5GJ/ton amino acid mixture from corn and 5.9GJ/ton

from wheat. These values have a direct function of the feedstock amino acid distribution and concentration. Wheat is less energy intensive in this respect as its resulting protein broth concentration is 8.1% versus 6.4% in corn. Afterwards, pure and isolated amino acids can be exposed to a wide multitude of biotechnological and biochemical technologies to produce final chemical products. Seeing that there are 20 amino acids present in varying concentrations, some potential production routes are less attractive. At this stage of biorefining only the 5 largest (mass-based) potential production routes will be selected for downstream processing while the residual amino acids will be subjected to decomposition to yield ammonia. The actual processing parameters are not fixed because the amine chemical processing steps are still in theory or in their laboratory infancy. The process energy requirements were based upon standard considerations as a function of the proposed process steps involved. Much like the isolation step, the exact amino acid concentration and internal distribution directly effects each process; a natural deviation exists from 5 to 35GJ/ton. Nevertheless, Table 2 lists the 5 potential chemical products from their respective amino acids along with the hypothesized processing steps and associated internal process energy demand from both the corn and wheat by-product feedstocks.

7.3.2.4 Intermediary Amino Acid Utilization

Preparing separate amino acid streams via protease digestion of the protein-rich by-products is the first step towards potential chemical production. For the essential amino acids (lysine, methionine, cystine, tryptophan, tyrosine, isoleucine, leucine, valine and phenylalanine) isolation and direct use as feed additives is a reasonable and viable product route. This route is advisable and feasible during the introduction phases, when the technologies and exact process layouts of the amine chemistry are under research and development. Furthermore, the isolation steps can be avoided when destined as an animal feed mixture additive, placing focus solely on effective protease digestion and separation.

7.3.2.5 Combined Heat and Power

In all proposed 2nd generation bioethanol production facilities combustion of the residual material in a combined heat and power (CHP) unit is included as a means to supply the necessary thermal and electric process energy[48]. Dried, distillers grains from the 1st generation systems could also be subjected to combustion in a CHP to reduce the overall process energy demand. In the above described amine chemistry utilization system, the residual unconverted material streams can be dried and combusted as well. In all of the various bioethanol layouts the residual streams can be used as a feedstock for the CHP unit. The various residual material streams need to be dried (down to $5\%_{moisture}$) to maximize the obtainable energy before being subjected to combustion. Drying some of the particularly wet streams is energy intensive, however, will still result in an increased overall energy output potential. The moisture content and the chemical composition of each residual material streams is different and will influence the bioenergy potential. The group contribution method together with typical drying requirements were used to determine the resulting calorific value of the residual material streams[19, 43].

Table 2   Amine Chemistry Overview

Amino Acid	Chemical Product	Yield* g/g	Distribution† %	Proposed Process Steps General Names	Energy GJ/ton
Corn Distillers Grains					
Leucine, Isoleucine	Isoprene	0.845	19.6	mevalonate biochemical pathway, enzymatic synthesis	14.2
Arginine, Glutamine, Glutamic Acid	1,4-Butandiamine	0.437	14.2	enzymatic hydrolysis, deamination, decarboxylation, amination reduction	22.5
Alanine, Aspartic Acid, Lysine	Ethylamine	0.435	11.6	enzymatic decarboxylation	17.8
Proline	γ-butyrolactone	0.668	16.8	oxidative decarboxylation	10.0
Phenylalanine & Tyrosine	Styrene	0.545	8.7	enzymatic deamination, thermal catalysis	10.5
Rest	Ammonia	0.193	29.1	amine reduction	21.6
Wheat Distillers Grains					
Arginine, Glutamine, Glutamic Acid	1,4-Butandiamine	0.437	19.6	enzymatic hydrolysis, deamination, decarboxylation, amination reduction	22.5
Leucine, Isoleucine	Isoprene	0.845	16.4	mevalonate biochemical pathway, enzymatic synthesis	14.2
Proline	γ-butyrolactone	0.668	11.4	oxidative decarboxylation	10.0
Phenylalanine & Tyrosine	Styrene	0.545	8.2	enzymatic deamination, thermal catalysis	10.5
Alanine, Aspartic Acid, Lysine	Ethylamine	0.435	6.5	enzymatic decarboxylation	17.8
Rest	Ammonia	0.193	37.9	amine reduction	18.1

*yield based on stoichiometric ratio and conversion rates
†product distribution in relation to proteins/amino acids

7.4 Results & Discussion

The chosen *impact assessment* results of the different system layouts for both crops are listed in full (see Table 3). The first row is dedicated to the bioethanol factories as they exist today; with the distillers grains marketed as an animal feed. Many studies have been conducted in recent years, especially for the corn-to-ethanol system, with a great fluctuation of results. Just recently National Geographic published its own feature on biofuels (*Green Dreams*[49]) and listed the collective US corn-to-ethanol industry as having a NEV of 1.3, which can be regarded as the current norm. In this analysis a higher NEV is expected as the system follows the best practice, however the resulting NEV was slightly lower at 1.2. There are three plausible factors leading to this deviation; firstly, a miscalculation between direct process energy and cumulative process energy for ethanol production, secondly, allocating DDGS to its calorific value instead of its animal feed mitigation potential and thirdly, the personal interpretation and influence on the methodology. Nonetheless, the figures are in the same vicinity and it can be said that both wheat-to-ethanol in Europe and corn-to-ethanol in America currently contribute to a (although minor) fossil fuel reduction. For sake of comparison and argument within the starch-to-ethanol system two other alternatives were studied; (1) combusting the DDGS and (2) the additional collection of stover/straw to combust it along with the DDGS. As can be seen in table 3 for both cases the value for all five categories

are worse. This means that as far as the 1st generation technology is concerned animal feed is better than burning.

Table 3   Resulting Fossil Fuel Savings

Generation	Description	Product Yield ton/ha*	NEV -	BF %	Fossil Fuel Saving (GJ)		
					/chem	/biomass	/ha
Corn	**USA - Iowa**						
1st	Ears only, DDGS used as feed	3.86	1.16	86.0	4.2	1.5	16.3
	Ears only, DDGS combusted		1.07	93.2	1.9	0.7	7.4
	DDGS and stover combusted		1.04	95.8	1.6	0.6	6.2
2nd	DDGS as feed, stover fermented and combusted	7.72	1.33	75.3	7.3	2.3	56.4
	WGS and stover fermented and combusted	8.20	1.39	71.7	8.5	2.8	70.1
Next	WGS and stover fermented and combusted, WGS protein extracted	7.98 + 0.34	1.62	61.7	12.0	4.8	117
	WGS and stover fermented and combusted, all protein extracted	7.98 + 1.59	1.39	71.7	16.3	2.8	156
Wheat	**EU - France**						
1st	Grains only, DDGS used as feed	2.26	1.39	71.8	9.6	2.7	21.8
	Grains only, DDGS combusted		1.24	80.7	5.9	1.6	13.3
	DDGS and straw combusted		1.11	90.3	3.8	1.0	8.6
2nd	DDGS as feed, straw fermented and combusted	4.36	1.58	63.4	12.3	2.9	53.8
	WGS and straw fermented and combusted	5.63	1.71	58.5	14.0	3.8	70.7
Next	WGS and straw fermented and combusted, WGS protein extracted	5.63 + 0.30	1.95	51.3	17.3	6.5	121
	WGS and straw fermented and combusted, all protein extracted	5.63 + 2.15	2.00	49.0	22.2	9.3	172.4

- NEV: Net Energy Value, no units
- BF: Breeding Factor, percentage
- WGS: Wet Distiller Grains with Solubles, not dried when used as lignocellulose feedstock
- Next: WGS protein extracted refers to actual protease solubility yields from initial experiments, all protein extracted future potential
- *Product yields ethanol, with "+" refer to extra amine chemicals

Expanding production by using the agricultural residues as an additional ethanol feedstock via the recent developments in 2nd generation technology does fulfil the expectations; more ethanol is produced and more fossil fuel is replaced. Three layouts were chosen for the 2nd generation system; (1) stover/straw as extra ethanol sources with residuals and ears/grains distillers grains combusted and (2) ear/grains distillers grains and stover/straw as extra ethanol sources with only the residuals combusted., and (3) stover/straw being the sole source of ethanol production with residual combustion as ear/grains are used for food processing. Around two-fold extra ethanol is produced from both cropping systems using the complex carbohydrates as an additional source of ethanol fermentation. The fossil fuel potential savings is also increased in all impact assessment categories. The *Green Dreams* feature also published data covering the various cellulose-to-ethanol production options and indicated a collective NEV range between 2 and 36, which depends on a variety of factors. None of the "cellulose" systems analysed herein achieved a NEV over 2 for there is one key difference in the system analysis. In the industrial biofuel research sector it is common practice to segregate data presentation and discussion between 1st and 2nd generation ethanol technologies. Typically in the 2nd generation sector data presentation is restricted to strictly agricultural wastes (considered free) and/or specifically grown woody biomass crops as feedstocks. This provides a convenient way to increase the contrast between 1st

and 2nd generation technologies, benefiting and supporting the validity of lignocellulose research. The US-corn and EU-wheat cases appear to have minimal effects as independently collecting the stover/straw only slightly increases the performance when compared to the combined cropping systems. Even if the feedstock was not allocated any energy input, the NEV figures (shown in table 2) would only increase by 34% for corn and 45% for wheat. Conversely, there is a decrease in the fossil fuel savings per land area category, due to the low biomass yield and respective ethanol production. Other dedicated lignocellulosic bioenergy crops (such as switchgrass) may score better in this impact category. In regards to the existing bioethanol industry it is unlikely that they will be decommissioned to make way for dedicated 2nd generation plants, an expansion is much more likely. In this study, the 1st generation by-product, distillers grains, is potentially used as an additional source of ethanol production linking the two technologies together, while attaining the desired increase in fossil fuel reduction.

The final two rows are dedicated to the so-called *"next"* generation in which the proteins are used for the additional preparation of chemical precursors. With this layout there are a multitude of products and a graphical representation is helpful[16] (see Figure 3). As complex as the graphic may appear it provides all the relevant data needed in calculating the values presented in table 3. Beginning with the agricultural fossil fuel input (right-hand side) the biomass components used for a product are assigned a mass allocated proportion. Each of the components follow their own independent production route with their described process energy demands. The final embedded fossil fuel energy costs for each product are grouped together and brought to a single value by basing the mass contribution of the final product array, thus acquiring the 14.4GJ/ton presented in the braces. This biorefinery energy cost is then compared with the cumulative process energy demand of the petrochemicals (left-hand side) they replace based on the same product distribution[50, 51], being 36.7GJ/ton. The system for corn is not shown seeing that the results in table 3 are listed and the graph would be similar. The resulting fossil fuel energy savings potential for both feedstocks is moderately better than the combined 2nd generation system. The reason for the moderate improvement is that 95% of the final product array is still ethanol. Listed in the bottom row of table 3 is the prospective fossil fuel energy savings should the protein separation techniques improve, lowering the relative ethanol product proportion to 72.3%. Here the saving difference is increased significantly, especially compared to the current 1st generation practices.
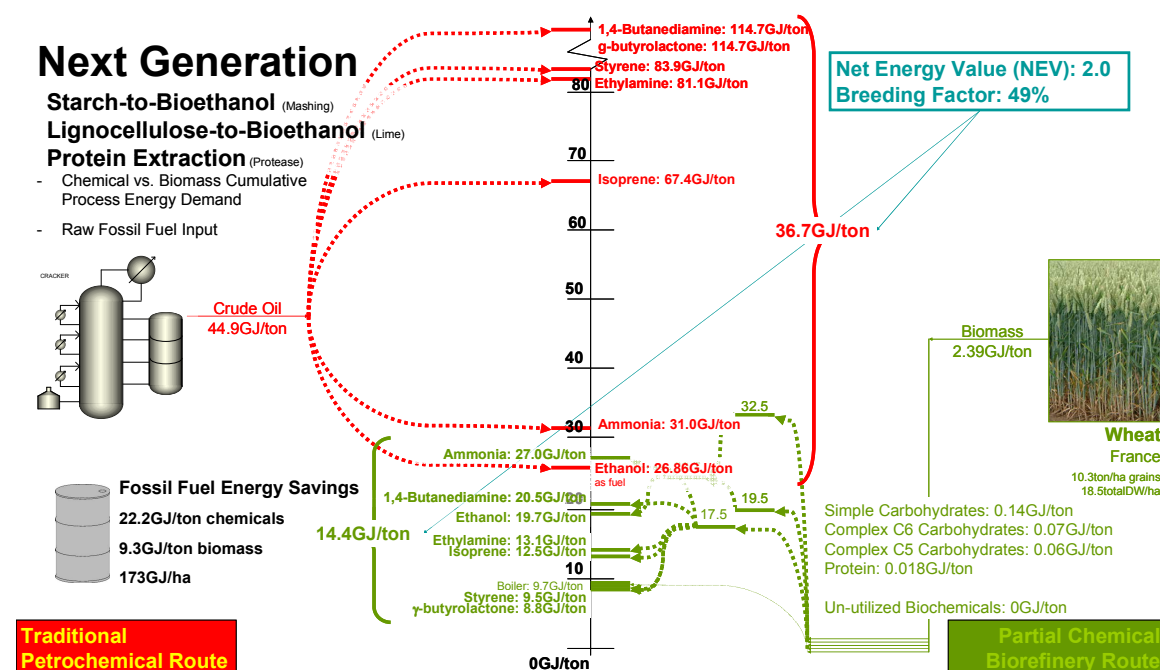
Figure 3 Fossil Fuel Savings
- Graphical representation of process energies relation between petrochemical route (red/left) and biorefinery (green/right)

Focusing solely on the net energy value indicates a rather modest improvement by expanding ethanol facilities to include lignocellulosic technology and amine chemistry. The relative improvement is 16% for corn and 14% for wheat, while assessing the potential savings per arable cropland reveals a much more depictive account of the improvement potential. Figure 4 illustrates the various system layouts for both crops with a clear trend; the bioethanol industry has plenty of room for further fossil fuel savings. Generally regarded as the lead cropping system in the world, the Brazilian sugar cane-to-ethanol is currently capable of mitigating 103GJ/ha by following the same methodological method[52]. Both the current US corn-to-ethanol and EU wheat-to-ethanol industries are well below this reference point, but by expanding to use the DDGS by-product with protein utilization, they are capable of surpassing this replacement potential. Following only the NEV as an indication factor would mislead, as the cane-ethanol is valued at 8.0, whereas even the potential chemical biorefinery cannot exceed 2.0[49]. The three categories chosen for the impact assessment provide a better insight into the potential increase in fossil fuel energy savings.

Continually supplying the biofuel industry with best practice yields is imperative to uphold high fossil fuel energy savings potential. Considering that yields can however deviate from year-to-year and from harvest-to-harvest, a sensitivity analysis can determine the consequences of a lower than expected biomass yield. For both US-corn and EU-wheat, current average yields are exactly 32% lower than the envisioned best practice yields. Pending lower yields, the potential fossil fuel savings for all biorefinery system layouts would decrease; the prospective next generation biorefinery for US-corn would decrease by 21.5% per chemicals and 46.7% per land use and the

133

EU-wheat would decrease by 6.3% per chemicals and 37.3% per land use. While these resulting figures are still overall higher than the lead biofuel cropping (Brazilian sugar cane) system, the drop in savings potential illustrates the susceptibility of yield disturbances. The sensitivity analysis has also been extended to incorporate average (or less than optimal) performances for each process step along the chain, including yields. The resulting reduction in fossil fuel energy savings is depicted by the minus error bars for the land use values in figure 4. They indicate an energy consumption trend for several of the 1st generation systems, but also reveal a substantial drop in the savings performance of the chemical generation to below the lead biofuel system. This has a strong impact on their potential contribution and in this regard stresses the importance of adhering to the best practice and striving for the maximum product conversion efficiency.
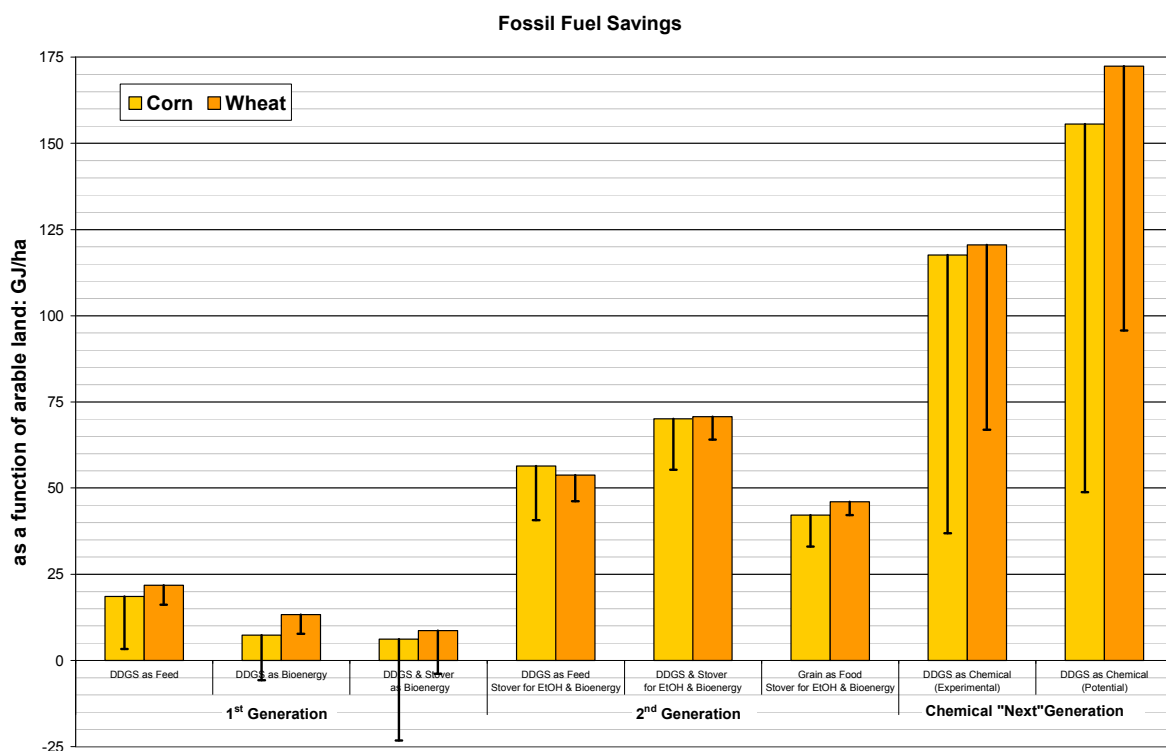
Figure 4   Fossil Fuel Savings as a Function of Arable Land

In regards to the US and EU operations, the potential fossil fuel mitigation leans towards wheat while the practical difference between them is negligible for all system layouts. Yet, there is one category where the US corn system clearly prevails, namely the product yields. Under today's system 72% more ethanol is produced per cultivated land area via the US corn route than the EU wheat route. Additionally, 64% more ethanol and slightly more amine-based chemicals (during the initial phases) are produced following the proposed biorefinery system. The land currently occupied by corn in the US is vast at 28.6 million hectares, but is equally vast for wheat within the EU-27 at 24.8 million hectares[27]. Given the land expansion restraints and the limited fossil

fuel energy savings difference from the analysed systems, US corn has and may very well have a stronger hold in the renewable energy sector.

7.5 Conclusion

The haste to develop an alternative (and renewable) transportation fuel has lead to a bioethanol industry that barely reduces the use of fossil fuels and is contributing to an imbalance in domestic feed markets. This contradicts the entire essence of renewability and what started in the US with corn has been mimicked in the EU with wheat in its place. They are still however, a crucial step forward in the right direction, which facilitates the options of improvements and expansions. Newer ethanol technologies are more energy efficient and can use existing by-products and agricultural residuals as additional feedstocks allowing for a larger proportional use of the biomass crop. Current production facilities can expand to incorporate these modern methods and as biotechnology continues to develop even other high added value co-products are imaginable. One such foreseeable and partly researched high value added option is applying amine biochemistry for the production of petrochemical precursors. Life cycle thinking and tools like cradle-to-factory gate assessments are invaluable to help steer governments policy and industrial research towards technologies that promote the decrease of fossil fuel intensity, thus becoming more renewable. The US corn-to-ethanol and EU wheat-to-ethanol can both increase their fossil fuel replacement potential several fold over by expanding to include lignocellulosic and protein separation improvement technologies. To achieve a mature bioethanol industry the renewability must be carefully assessed and maximized without causing other unwanted disturbances.

7

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Maximum fossil fuel feedstock replacement potential of
petrochemicals via biorefineries

8

Abstract

The search for feedstock replacement options within the petrochemical industry should logically be based upon non-fossil resources. Retaining the functionality of the biochemicals in biomass for use as chemical products and precursors can lead to a sizeable reduction of fossil fuel consumption. This was assessed by using a limited energetic and exergetic cradle-to-factory gate analysis following the principles of life cycle assessments (LCA). A calculation matrix was created for 16 bioenergy crops in their corresponding regions and for a conceptual biorefinery oriented towards existing bulk-chemical products. The optimal biorefinery cropping system was determined according to the fossil fuel mitigation efficiency in relation to chemical feedstock products and land use consumption. The "worst" performer still has a replacement potential of $22.2GJ_{energy}/ton_{product}$ and $125GJ_{energy}/ha$ while the "best" performer can achieve $50.8GJ_{energy}/ton_{product}$ and $721GJ_{energy}/ha$. In addition to energy, exergy evaluation was included, to indicate potential areas of energy efficiency improvement. The combined evaluations demonstrate that the highest potential of biomass to replace fossil fuel resources is as an alterative feedstock source in the petrochemical industry.

Keywords

LCA, Petrochemical Industry, Alternative Feedstock, Biomass, Biorefinery

8.1 Introduction

Matthew Simmons, a prominent oil-industry insider and expert, stated in the documentary film *"A Crude Awakening"* that the world is approaching the age of reduced global crude oil production, with mid-2007 likely to have given the maximum production[1]. Originally proposed and investigated for all fossil fuels by M.K. Hubbert in 1956[2], this date was then described as *"the date of the culmination"*. Today it is more commonly referred to as *"Hubbert's Peak"* or simply *"peak oil"*. In Kenneth S. Deffeyes' recent book and regularly updated website, he claims that world peak oil already occurred as of December 16th, 2005[3, 4]. Whilst this is debatable, it does correspond well with the current spiralling trend of the world oil market price; hence realization, not speculation as often claimed.

The bulk of the energy sector is composed of petroleum plus the other fossil fuels, and while the petro*chemical* industry is frequently neglected in most studies, the combined chemical industry consumes 7.8% of total OECD energy production [5]. The petrochemical industry relies upon fossil-based feedstock (primarily naphtha and natural gas) and an array of all fossil fuels to generate the required process energy. Electricity and other material requirements are often recorded as direct purchases (i.e. kWh and tons) and not related to the indirect energy involved in their respective production, meaning the total proportion of the energy sector is likely higher.

A wide multitude of alternative energy replacement options already exist. More recently however, as the issue of climate change has become more prominent on the global agenda, there is further incentive for the replacement of fossil fuels to be by CO_2 neutral sources in order to achieve an overall reduction of greenhouse gas emissions (GHG)[6].

Feedstock replacement options for the petrochemical industry should logically be based on non-fossil resources, potentially alleviating the issue of peak oil, instable prices and reducing the impact on global climate. The fossil feedstock used as raw materials for product may not immediately end up as GHG emissions, but for example in the Netherlands, only 5.9% household and 11.2% industrial waste is permanently landfilled meaning the rest will eventually end up as air emissions via incineration [7]. Therefore, also feedstock replacement is relevant for carbon neutrality. Biomass is a potential feedstock, which due to the general notion of carbon neutrality, has received much attention. Its potential carbon dioxide and other greenhouse gas emissions reduction is currently under scrutiny and is said to be significantly less than previously anticipated[8]. Despite this dispute, biomass has an exceedingly more important attribute of relevance to the petrochemical industry; its complex carbon backbone and existing chemical functionality[9]. Utilizing these biochemical configurations for synthesizing functional chemical products can significantly reduce the energy required along the chemical synthesis chain.

Practically all existing studies investigating biomass as an alternative energy source focus on its potential as a replacement for the heat and power generation (bioenergy) and the transportation

(biofuels) categories of the energy sector. While fewer, some studies are focused on biochemicals but, are typically written for "green" chemicals with new and unique properties preventing integrated market entry in the existing petrochemical industry. Producing existing chemicals from biomass should be the focus with such studies greatly limited.

The chemical industry has, however, already begun to seriously contemplate the long-term feedstock replacement potential of biomass over existing and other fossil fuels [10]. While these studies are based on standard 1st generation biofuel technology, they present a necessary starting point. Biofuels will undoubtedly help pave the developmental path towards more complex chemical biorefineries.

Chemical biorefineries will have a considerably large fossil fuel reduction potential and help ensure the sustainability of the chemical sector. It is also likely to be the most effective use of biomass to replace the fossil fuel component in the grand energy sector. Validating this statement is imperative, requiring sound methodological assessment. This poses a unique challenge due to the variety in biomass types, cultivation regions, and conceptual biorefinery layouts. Assessing biorefineries for their fossil fuel replacement potential must therefore be highly contextualized. This paper outlines the created calculation matrix, following the principles of life cycle assessments (LCA's), to determine the optimal biorefinery cropping system for replacing the petrochemical industry's fossil fuel consumption both directly as a feedstock and indirectly as process energy. The calculation matrix is used for a selection of different biomass types in different geographical regions subjected to different conversion technologies to yield the same array of existing petrochemical products. The total embedded fossil fuel energy (and exergy) for each aspect within the calculation matrix has been specified in a contextualized fashion. Finally, the question of whether the most efficient use of biomass is for chemical feedstock production, as chemical biorefineries, will be answered.

8.2 Methodology

The construct, procedure, and methodology of the calculation matrix was fully described in a previous article[11]. The assessment can be succinctly summarized as a *"limited energetic and exergetic cradle-to-factory gate analysis"*, which assesses the entire production chain for identical chemical products originating from both the traditional petrochemical route and from the potential biomass route. The chains are investigated for their material and energy inputs from the initial point of exploration/extraction and finally related to the total amount of imbedded fossil fuel energy; which is the total *cumulative energy consumption* (CEC). Inclusion of the thermodynamically efficient usage value of energy, *exergy*, was performed to indicate possible improvement options[12]. Determining exergy values necessitates a more in-depth knowledge of the processes along the production chains over the general information provided by traditional LCI databases. This is demonstrated in the sulphur and phosphorous nutrient issue[13]. Sulphur was generally regarded as an energy-free by-product from oil refining. Therefore, following detailed assessment biomass had previously been assigned a negative energy/exergy input component from both the sulphur

and phosphorous nutrients. Although rather recently, several LCI software database add-ons have been created especially for the field of bioenergy which may facilitate good and consistent LCA's, they were not used in this assessment, as adhering to detailed methodological description[14].

The matrix calculations facilitate the determination of the total embedded fossil fuel energy and its efficient utilization (exergy) for a variety of biomass feedstock production configurations in relation to the traditional petrochemical feedstock production. As mentioned in a previous article (focused on a single biomass type and product [15]), the best *impact assessment* terms for sustainability issues are:

- fossil fuel energy savings per bio-chemical mixture produced $(GJ/ton_{chemical})$,
- fossil fuel savings per annually harvested biomass $(GJ/ton_{biomass})$ and,
- fossil fuel savings per arable land area (GJ/ha)

Savings per chemicals produced and savings per occupied arable land are of special interest for biomass production chains; they express the fossil fuel replacement potential efficiency of the chemical feedstock products and land consumption. Both resulting values were normalised (in relation to the minimum and maximum values) and plotted against each other, which was used to determine the optimal biorefinery cropping system.

8.3 Calculation Matrix

8.3.1 Biomass Crop Choice

The first step in the assessment is creating a list of bioenergy crops by making a selection of those in regions of fast growth, high yields, generally low agricultural intensity, and with a high degree of familiarity. Several crops fit this portfolio and are topical in biobased economy discussions, hence the term *bioenergy crops*. Although there are many more crops, listed in Table 1 are 16 choice bioenergy crops and their corresponding regions of cultivation. They vary by nature and type; sugar-rich, oil-rich, temperate, tropical, etc. While several online databases were used to amass the majority of the data[16-22], other information was retrieved from a wide variety of sources (not specifically listed). The first data presented in table 1 is the biomass yields as handled in agronomy; at low, average and best practice. The difference between regional average and best practice for common crops cultivated in prosperous areas with a long tradition reveals a 1.6 fold increase with a standard deviation of only 18.6%. Both the increase and the standard deviation are higher in developing areas. Supplying biomass consistently and over prolonged periods to biorefineries will have to derive from best practice cultivations. Furthermore, in non-food applications the entire crop (minus non-usable rooting structure), i.e., the total dry weight yield (tonDW/ha/a) will be utilised. Overall material yields directly influence values along the chains of the analysis. Although, there is a general preference for higher yields, a lower yielding crop might contain a high concentration of chemicals benefiting the biorefinery concept. Figure 1 illustrates the relative biochemical composition of the select bioenergy crops including ash

(minerals and inorganics). Figure 2 illustrates the amino acid distribution of the proteinaceous content, which is directly related to the amine chemistry section of the biorefinery.
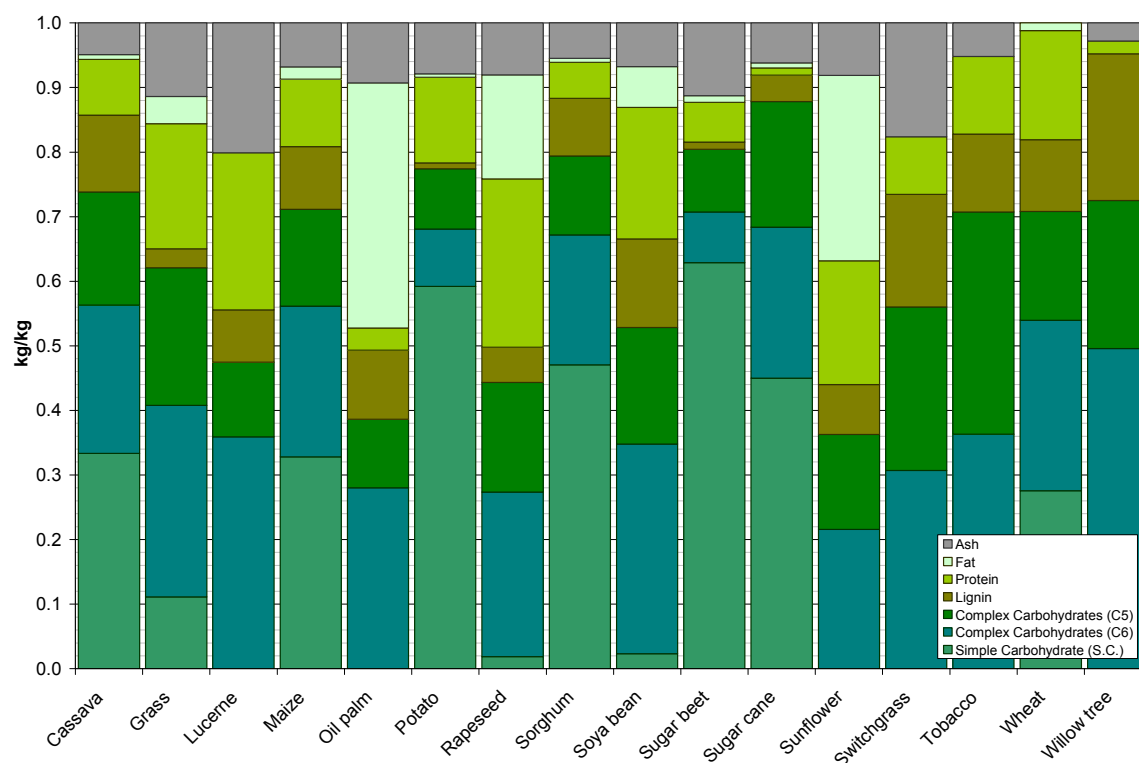
Figure 1   Select Biomass Biochemical Composition Proportions

8.3.2   *Agricultural Energy Input*

The *agricultural energy input* is a summation of all input categories requiring fossil fuel energy to cultivate, harvest and deliver the biomass to the biorefinery. There are four major categories regarding inputs on the field (fertilizers, pesticides, irrigation and farming practices) and three for logistics (sizing/drying, transport and storage/handling). As mentioned in the methods section, the details pertaining to the calculations are described elsewhere[11]. A good overview of the agricultural energy input related to the field was compiled for EU-wheat and US-corn[23]. A significantly more detailed assessment was performed, following the same procedure, for sugar cane in Brazil with a focus on achieving best practice over average yields [15]. The best practice yields conditions are taken here into account for all choice bioenergy crops.

The biomass is envisioned to be delivered to a large petrochemical cluster (or centralized processing area) such as Houston, Singapore or in this case Rotterdam. Fresh biomass cannot be transported effectively: it often contains large quantities of water (i.e. WW vs. DW), is irregular in shape and therefore has a low net packing density, and left untreated can rapidly spoil (material and/or quality loss). Thus, shipping biomass in it native form to the centralized biorefinery is not

effective. Figure 3 presents a simplified process flow diagram (PFD) of the general processing stages for all biomass crops. The dehydration unit is the last stage of on-site (small-scale) processing, before shipping to the centralized (large-scale) processing cluster. On-site or close-to-farm processing is desired for the crops cultivated well beyond the hinterland area of the cluster. After separation of ethanol, the half-product mixture is dehydrated and transported along with the other near final products (ethylene, PDO, etc.) to the large-scale centralized biorefinery. This may entail pipelines, specialised trucks, and/or train compartments, but is dependent on the local logistic possibilities. Local or on-site situation of some of the bulkiest and most low-value steps vastly lowers the logistics component of the agricultural energy input. Sizing, drying and handling are a function of the supply chain employed. Parameters are optimised for the Rotterdam choice, but are not covered in detail. Table 2 lists the total agricultural fossil fuel input energy necessary for all categories to supply both the locally produced chemical products and the centrally produced components.

While each category is individually listed in land terms (GJ/ha) the total combined value is listed in yield terms (GJ/tonDW).
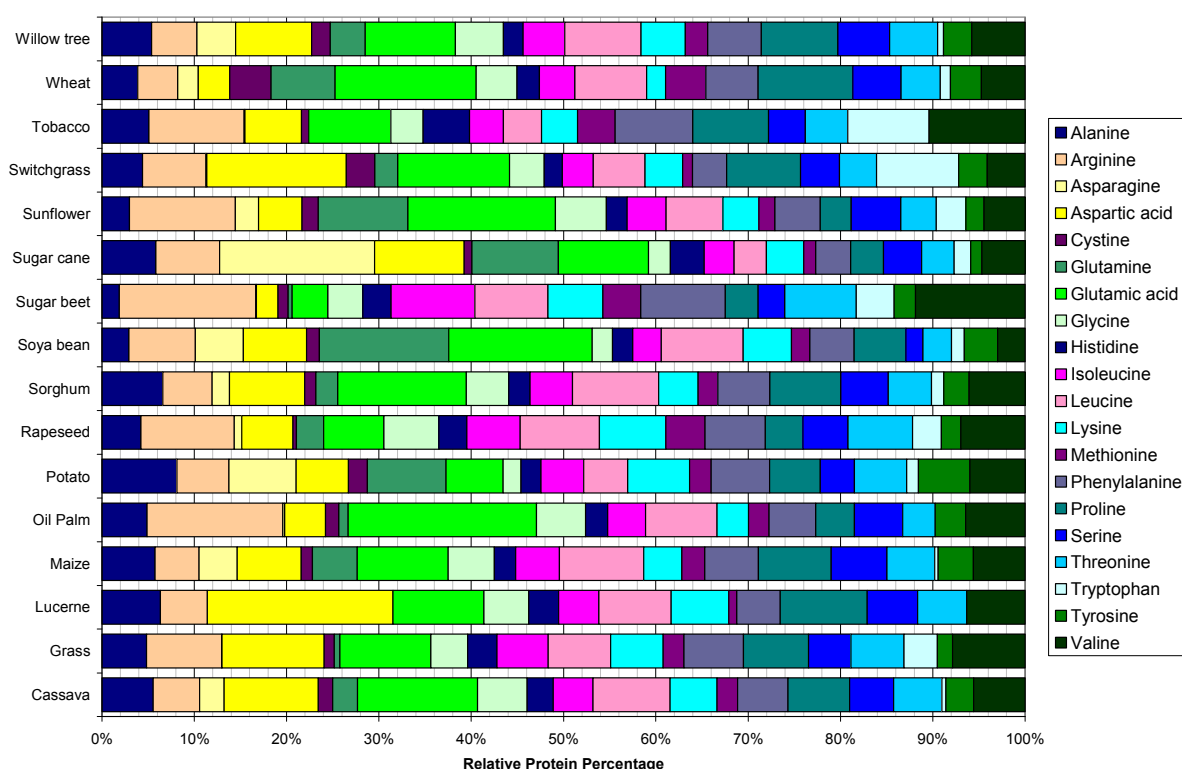
Figure 2   Total Bioenergy Crop Amino Acid Distribution

8.3.3   Biorefinery Energy Input

Figure 3 briefly outlined the products to be expected in a biorefinery. Each biochemical component present in biomass will undergo the necessary processing steps to produce one or more chemical products. This basically means that biofuels are not produced (even though there are many overlapping process routes) and that bioenergy (heat and power) is only produced from residuals and those components in too low concentrations to warrant specified processing. The selected end products should be existing bulk-chemicals (1st to 5th derivates) which can be produced from biomass with moderate levels of continued research and development. Exceptions are the amine and lignin processing routes, which are still based on hypothetical or experimental processes.
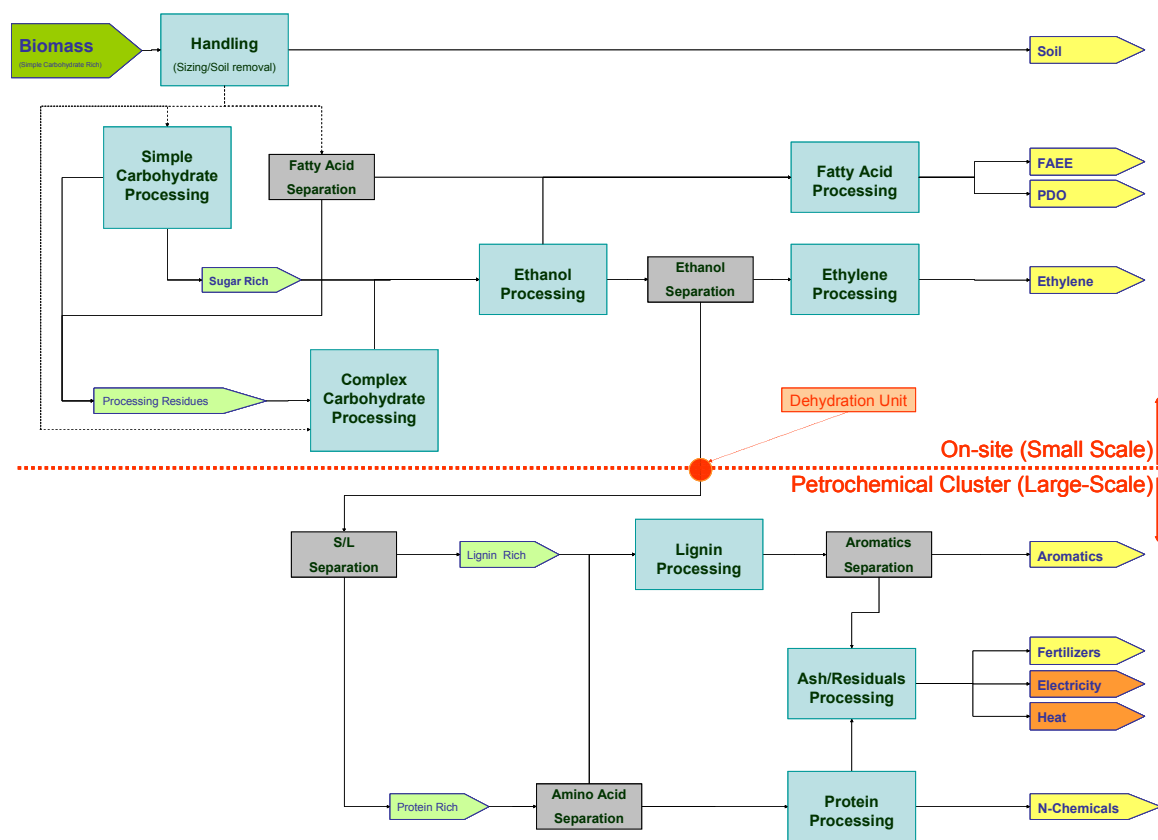
Figure 3   Overview Biorefinery with On-site and Petrochemical Cluster Production
- After the handling stage there are three options depending on the crop type and biochemical composition
1. Crops containing levels above 20% total crop proportion of simple carbohydrates are subjected to its processing stage
2. Crop containing levels above 5% total crop proportion of fats are subjected to fatty acid separation and its processing stage
3. Crop with levels below (1) and (2) are fed directly to the complex carbohydrate processing stage

Each processing stage is evaluated for the direct electric, direct thermal energy and exergy consumption along with the cumulative energy/exergy consumption of the indirect sources (i.e. chemicals, enzymes). The stages are categorized on crop type dependencies, following both standard processes and expected best practice procedures. The (energy and exergy) costs for

Table 1 Selected Biomass Crop and Regional Production Location with Associated Biomass Yields

Crop	Largest Producer		Arbitrary Starting Location*			Biomass Yields				
Name	Continent	Country	Latitude	Longitude	Village/Town	Agricultural Term†	Low	Average	Best Practice	Total DW‡
Cassava	Africa	Nigeria	8	7	Minna	Tuber	8.0	9.4	50.0	35.1
Grass	Europe	Holland	51	5	Raalte	Dry Biomass	10.0	12.5	14.1	14.1
Lucerne	North America	South Dakota	44	-103	Gettysburg	Dry Biomass	1.3	4.5	15.0	15.0
Maize	North America	Iowa	41	-91	Kalona	Grain	2.8	9.0	13.8	24.8
Oil palm	South Pacific	Malaysia	2	113	Kapit	Fruit/Seed	10.0	19.5	25.0	34.5
Potato	Europe	Holland	51	5	Raalte	Tuber	20.0	43.5	65.0	17.5
Rapeseed	Europe	Belgium	50	5	Hannut	Seed	3.0	3.8	5.5	16.4
Sorghum	Africa	Kenya	0	35	Chemelil	Green Biomass	25.0	35.0	75.0	36.9
Soya bean	North America	Illinois	41	-90	Fair Haven	Seed	1.7	2.6	4.0	10.8
Sugar beet	Europe	Germany	52	8	Uchte	Tuber	30.0	57.6	100.0	29.2
Sugar cane	South America	Brazil	-25	-50	Pres. Prudente	Cane	15.0	72.3	125.0	43.5
Sunflower	Europe	France	48	0	Yevres	Seed	1.2	2.3	5.5	8.4
Switchgrass	North America	Iowa	41	-91	Kalona	Dry Biomass	3.1	8.1	14.0	14.0
Tobacco	South Pacific	Australia	-34	145	Annuello	Dry Biomass	4.0	24.0	26.5	26.5
Wheat	Europe	France	48	0	Yevres	Grain	6.0	7.0	10.3	18.6
Willow tree	Europe	Sweden	56	13	Starby	Dry Biomass	3.0	4.5	8.0	8.0

*Starting point of the logistics layout, nearest village/town within the ca. 100km x 100km coordinates
†Term included in governmental and regional statistics, relevant for the agricultural industry
‡Total dry weight, including stem, stover, leafs, all residue above soil biomass, etc. on a yearly basis with a 10 year averaged value

Table 2   Total Agricultural Fossil Fuel Energy/Exergy Input of Propagation and Delivered Biomass

Crop	Fertilizers		Pesticides		Irrigation		Farming		Sizing/Drying		Transportation		Storage/Transfer		Total (GJ/tonDW)*	
	Energy	Exergy	En	Ex	En	Ex	En	Ex	En	Ex	En	Ex	En	Ex	Energy	Exergy
Cassava	16.5	18.3	0.0	0.0	0.0	0.0	2.5	2.5	12.9	15.2	28.7	28.6	1.4	1.4	1.92	2.04
Grass	13.5	15.3	0.3	0.3	1.1	1.1	7.3	7.4	9.2	10.8	2.6	2.6	0.3	0.3	2.45	2.70
Lucerne	11.9	13.8	0.1	0.1	22.9	29.4	6.6	6.7	10.2	12.0	25.1	25.0	0.2	0.2	5.17	5.86
Maize	16.7	18.7	1.3	1.4	2.3	2.9	3.3	3.4	11.0	12.9	18.6	18.6	2.2	2.3	2.26	2.46
Oil palm	13.1	14.5	0.7	0.8	0.0	0.0	2.2	2.2	12.5	14.7	52.5	52.4	2.2	2.4	2.50	2.61
Potato	13.3	14.7	3.7	3.9	0.1	0.1	8.6	8.6	6.1	7.1	2.3	2.3	0.9	0.9	2.04	2.21
Rapeseed	21.3	23.3	1.0	1.1	0.0	0.0	3.2	3.2	9.3	11.0	2.4	2.6	1.5	1.5	2.45	2.69
Sorghum	16.8	18.5	0.0	0.0	0.0	0.0	9.2	9.1	12.0	14.1	31.7	31.6	0.4	0.5	2.05	2.16
Soya bean	1.0	3.5	0.6	0.6	5.2	6.6	3.0	3.0	6.3	7.4	12.6	12.6	0.5	0.5	2.77	3.26
Sugar beet	25.7	28.4	1.6	1.7	3.6	4.7	6.6	6.6	10.0	11.8	6.0	5.9	2.6	2.6	1.97	2.17
Sugar cane	4.6	5.2	1.9	2.0	0.1	0.1	2.9	3.0	12.5	14.7	30.5	30.4	4.6	4.7	1.34	1.41
Sunflower	16.7	18.9	0.5	0.5	10.5	13.5	5.6	5.7	4.1	4.8	1.4	1.5	0.5	0.5	4.85	5.60
Switchgrass	17.4	19.4	0.2	0.2	0.0	0.0	5.6	5.7	8.3	9.8	11.3	11.3	0.3	0.3	3.11	3.37
Tobacco	20.5	22.4	6.2	6.6	0.0	0.0	9.3	9.5	12.0	14.1	41.0	41.3	1.0	1.0	3.43	3.61
Wheat	18.1	19.9	0.9	1.0	2.1	2.7	3.5	3.5	9.0	10.6	3.1	3.3	0.7	0.7	2.04	2.27
Willow tree	12.2	13.8	2.1	2.2	0.5	0.6	3.1	3.2	3.4	4.0	1.9	1.9	0.3	0.3	2.98	3.30

Values in GJ/ha/a
*Total includes transfer and handling yield losses, not presented

construction of the biorefinery plants were evaluated (using LCI databases) and included, but were found represents just a fraction of a percent.

The processing considerations will be highlighted in details for eight major processing stages: 1. simple carbohydrates, 2. complex carbohydrates, 3. ethanol, 4. ethylene, 5. fatty acids, 6. amino acids, 7. lignin and, 8. ash.

8.3.3.1 Simple Carbohydrates Processing

Simple carbohydrates are those carbohydrates that are readily converted into glucose, fructose or equivalent molecules. The crops that contain sufficiently high levels of simple carbohydrates are categorized into two groups; starch-rich and sucrose-rich crops. A further division was made between crop types as they have distinctive processing steps and thus energy demands. The processes are based in large on standard bioethanol technology[24]. Other crop specific studies provide useful data for the simple carbohydrate processing stage as a whole[25]. Recent modifications and studies have revealed energy efficiency improvements[26, 27] in existing plants. Table 3 presents the resulting and relevant figures for inclusion in the biorefinery calculation matrix.

Table 3   Process Energy/Exergy Input – Simple Carbohydrates to Fermentable Sugars

Category	Starch-Rich			Sucrose-Rich	
Crop Type	Cereals	Cereals (corn)	Tuberous	Stems	Bulbs
Conversion Rate (%)	96.2	97.7	99.2	94.9	95.1
Electric Energy (GJ/ton)	0.256	0.260	0.198	0.452	0.069
Thermal Energy/Exergy (GJ/ton)	0.52/0.02	0.99/0.10	2.51/0.43	-/-	0.89/0.15
Indirect Energy/Exergy (GJ/ton)	0.11/0.11	0.11/0.11	0.11/0.11	-/-	-/-

- Product fermentable sugars (glucose, fructose, etc.)

8.3.3.2 Complex Carbohydrates Processing

Complex carbohydrates are largely understood as cellulose and hemicellulose, but are any polysaccharides based on C6 and C5 moieties. In this processing stage all C5 and C6 sugars will be handled together, although conversion rates will be individually specified. Over the past decades many pretreatment technologies, required for downstream fermentation, have been made investigated[28]. They all have their own process dynamics, optimal conversion rates, energy intensity and feedstock preference. These biomass feedstock types can best be separated into 3 groups;

- Agricultural wastes (fresh biomass like stover)
- Process residues (press cakes and distillers grains from simple carbohydrates processing)
- Recalcitrant material (woody material with high lignin content above 15%)

The optimal pre-treatment technology for each of these biomass types was assessed based on energy investment (direct and indirect) in relation to the product yield, striving for the lowest GJ per ton released sugars. A systematic calculation model was created for all current technology options for each feedstock using several studies and process models, both externally and internally[29, 30]. Table 4 lists the selected pre-treatment technologies, their associated conditions

and resulting process energy/exergy requirements. For agricultural wastes, unexpectedly high yields were achieved using steam pretreatment[31, 32]. A more systematic approach was performed on assessing the ammonia fast explosion (AFEX) process with a quench ammonia recycling system[33]. This pre-treatment proves quite effective on process residues, like corn distillers grains[34]. Dilute acid (most studied) appears to work well on high lignin feedstocks, albeit at severe conditions[35, 36].

Table 4   Process Energy/Exergy Input – Complex Carbohydrates to Fermentable Sugars

Category	Agricultural Wastes	Process Residues	Recalcitrant Material
Pretreatment Technology	Steam	AFEX	Dilute Sulphuric Acid
C6 Conversion Rate (%)	95.9	91.3	94.0
C5 Conversion Rate (%)	93.8	86.3	95.0
Process Conditions (°C/bar/min)	210/20/5	100/20/5	160/12/20
Electric Energy (GJ/ton)	0.01	0.15	0.07
Thermal Energy/Exergy (GJ/ton)	2.24/0.62	0.96/0.20	0.64/0.14
Indirect Energy/Exergy (GJ/ton)	0.94/1.13	2.32/2.74	2.82/3.42

- C6 carbohydrates: cellulose, pectin, mannose, galactose
- C5 carbohydrates: hemicellulose, arabinose
- Product fermentable sugars (i.e. glucose, xylose)

8.3.3.3   Ethanol Processing

Both simple carbohydrates and complex carbohydrates are subjected to ethanol fermentation to produce ethanol. Glucose, xylose and other saccharides are readily converted into ethanol at a fixed stoichiometric rate of 0.512kg/kg. Many existing fermentation and separation process can be classified as state-of-the-art, but a selection of recent improvements is nonetheless included to lower the energy intensity further. For example, use of molecular sieves drastically reduces the energy intensity of the ethanol dehydration process. While they are only employed in newer plants they are considered as the standard. Modern nanoporous dehydration membranes can achieve higher purities (beneficial for further processing into ethylene) at lower energy costs[37]. The use of solid state fermentation (SSF) and thermotolerant yeasts and microorganisms both result is a significant reduction of thermal energy demand in separation[38, 39]. The *SSF-biostil* process further reduces the separation cost by using a portion of the rectifier product as a stripping medium in the beer column[40]. Table 5 lists the results for both the standard and recent select; the recent select values are used in the matrix.

Table 5   Process Energy/Exergy Input – Fermentable Sugars to Ethanol

Process Technology	Standard	Recent Selection
C6 Conversion Rate (%)	95.9	95.8
C5 Conversion Rate (%)	89.9	89.8
Electric Energy (GJ/ton)	0.46	1.66
Thermal Energy/Exergy (GJ/ton)	5.19/0.99	3.16/0.13
Indirect Energy/Exergy (GJ/ton)	0.17/0.21	0.17/0.21

- C6 sugars: glucose
- C5 sugars: xylose

8.3.3.4 Ethylene Processing

Ethylene can easily be produced by the well established ethanol dehydration process[41]. Newly developed solid-acid catalysts such as zeolites or silica-alumina configurations have lowered the energy intensity and improved the conversion rates[42]. Strictly following the stoichiometric, 1.64 ton of ethanol per ton of ethylene is required, however when taking all efficiencies into account 1.67 ton/ton is needed or 59.8% conversion. The required process energy for the zeolite system is listed in Table 6.

Table 6   Process Energy/Exergy Input – Ethanol to Ethylene

Process Technology	Adsorbing Zeolites
Conversion Rate (%)	59.8
Electric Energy (GJ/ton)	0.30
Thermal Energy/Exergy (GJ/ton)	1.17/0.26
Indirect Energy/Exergy (GJ/ton)	-/-

8.3.3.5 Fatty Acid Processing

Fatty acids can be easily converted into biodiesel, oily products such as lubricants (biolubricants) or similar components suitable for blending. Standard methods for producing biodiesel employ pressing, extraction, transesterification, and purification steps[43-45]. Several improvements are however feasible. Instead of relying on imported methanol from natural gas, internally produced ethanol can be used. The ethanol costs cannot be displayed here as it is a function of the final biorefinery layout. Using ethanol, one produces fatty acid ethyl esters (FAEE), which can be readily used as a biolubricant. Glycerol is an abundant by-product which will make an excellent feedstock for 1,3-propanediol (PDO) thus optimally utilizing the existing C3 structure of glycerol[46]. Other components cannot be converted at the same level of efficiency. Table 7 lists the results.

Table 7   Process Energy/Exergy Input – Oils to Fatty Acid Ethyl Ester

Category	Seeds		Fruits	
Process Technology	Standard	Altered	Standard	Altered
Conversion Rate (%)	89.8	94.0	90.3	94.6
Electric Energy (GJ/ton)	0.18	0.43	0.37	0.62
Thermal Energy/Exergy (GJ/ton)	3.41/0.34	2.33/0.23	9.34/0.93	4.21/0.42
Indirect Energy/Exergy (GJ/ton)	4.13/4.30	2.19/1.90	4.19/4.37	2.17/1.86

- Also produces PDO at 53.9kg/ton seed-based and 55.5kg/ton fruit-based

8.3.3.6 Amino Acid Processing

It has been argued that the structure of amino acids can be of great benefit for the production of nitrogen-containing chemicals by contributing to an increased overall fossil fuel replacement potential within biorefineries[9, 23, 47]. Downstream processing should align their unique structure to that of the final product. The functional groups, predominantly nitrogen, are thus best maintained where possible. The conventional option of using the protein fraction as animal feed is never optimal, but in some cases may still be an intermediary solution. The field of protein

based synthesis is still however very much in development, and therefore process concepts still in the research and development phase must be considered[48].

The first step is disclosing the fraction from the residual biomass and separating it. This is effectively performed by enzymatic hydrolysis into amino acids using proteases: this preserves the functionality of the amino acids while removing the specific functionality of the proteins, which facilitates further processing[33, 49].

Following separation the physiochemical properties of the amino acids, most notably molecular size, charge and hydrophobicity (solubility) are used for subsequent fractionation[50, 51]. Figure 4 shows a possible (but not necessarily best) configuration for amino acid fractionation which will form the basis of further assumptions and calculations. Electrodialysis (ED), although intensive in electric power usage, is chosen as a first step because amino acid fractionation using ED is closest to maturity (e.g., isoelectric focusing is an existing albeit not yet commercialized process). Another option could be fractionation based on size and charge using a cascade of nanofiltration units or chromatographic stream polishing for the final purification step. The chosen conceptual set-up is focused on a high rate of fractionation with a relatively low energy intensity using readily available technology. There are countless other options, combinations, and unforeseen future developments that can be expected to achieve a higher fractionation performance. Nevertheless, its combined technology is advanced and complex. It will only be realistic in the near future at a centralized processing facility (i.e. the earlier mentioned petrochemical cluster).

8

After isolation the amino acids can be subjected to a variety of synthesis routes to create an array of chemical products. Most of the products shown in Table 8 are based on an earlier mini-review[47]. These existing processes and plausible process routes were taken from biochemistry, medicine and in some case metabolic pathways studies. Other hypothetical amino acids production routes are:

- from arginine to ornithine via enzymatic hydrolysis[47, 52]
- from ornithine to butanediamine via enzymatic decarboxylation[53]
- from glutamine to glutamic acid via enzymatic deamination hydrolysis[54]
- from γ-amino butyric acid (GABA) to butanediamine using the reverse reaction of reductive deamination via standard amination[55]
- from histidine to ionic liquids via the idea of solution dissociation
- from leucine and isoleucine to isoprene via the complex biosynthesis mevalonate pathway and enzymatic synthesis[47, 56]
- from lysine to ε-caprolactam via thermal degradation to α-amino-ε-caprolactam followed by an enzymatic deamination[57]
- from tryptophan to adipic acid via a hydrogenation step of intermediary muconic acid[58].

Table 8 provides an overview of a single chemical product portfolio using these synthesis routes. The listed routes and products do not represent the best technique or chemical direction; they are only chosen as an indication. The exact processing conditions cannot be given, since are not product specific enough yet to be determined for a single product. Similar reaction/synthesis steps involved were grouped together for calculation: decarboxylation, hydrolysis, Maillard reaction, amination, electrolysis, fermentative degradation, enzymatic catalysis, deamination and removal of water (evaporation).
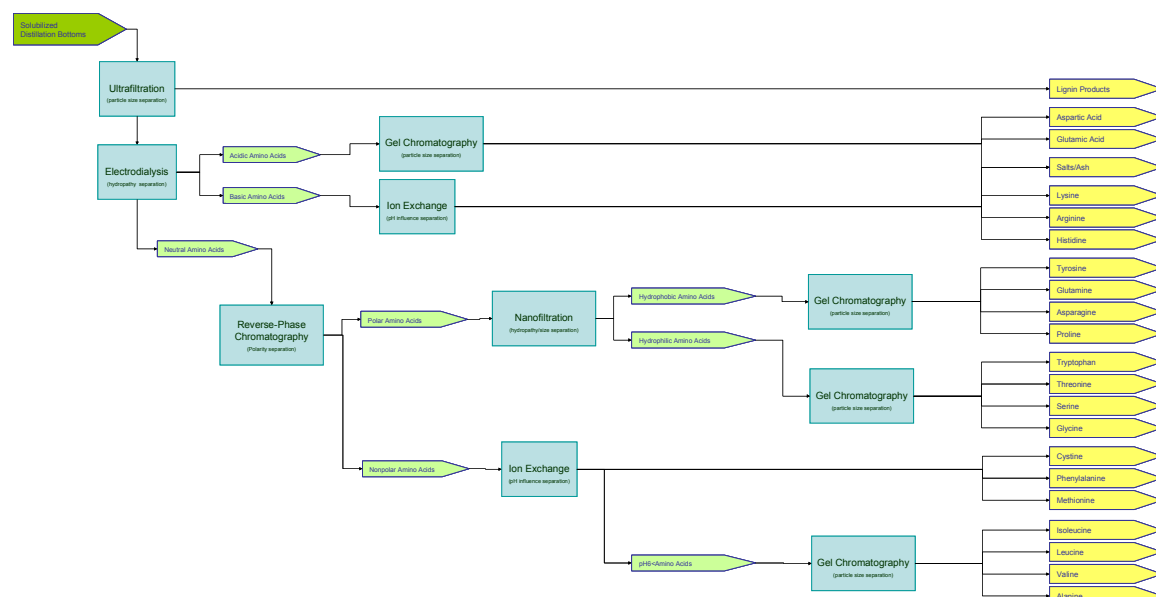
Figure 4   Possible Amino Acid Separation and Purification Step

Table 8   Overview of Potential Amino Acid Chemical Derivates

| Amino Acids					Products							
Nomenclature	Symbol	Formula	Structure	Molecular Mass	Primary	Formula	Structure	Yield	Secondary	Formula	Structure	Yield
Alanine	ala	$C_3H_7NO_2$		89.1	ethylamine	C_2H_7N		0.51				
Arginine	arg	$C_6H_{14}N_4O_2$		174.2	1,4-butandiamine	$C_4H_{12}N_2$		0.46	urea	$(NH_2)_2CO$		0.31
Asparagine	asn	$C_4H_6NO_4$		132.12	acrylamide	C_3H_5NO		0.54				
Aspartic acid	asp	$C_4H_7NO_4$		133.1	ethylamine	C_2H_7N		0.34				
Cysteine	cys	$C_3H_6NO_2S$		121.16	feed grade cysteine	$C_3H_6NO_2S$		1.00				
Glutamine	gln	$C_5H_{10}N_2O_3$		146.15	1,4-butandiamine	$C_4H_{12}N_2$		0.46				
Glutamic acid	glu	$C_5H_9NO_4$		147.13	1,4-butandiamine	$C_4H_{12}N_2$		0.51				
Glycine	gly	$C_2H_5NO_2$		75.07	oxalic acid	$C_2H_2O_4$		0.65	ammonia	NH_3		0.12
Histidine	his	$C_6H_9N_3O_2$		155.16	ionic liquids	$C_2H_5NH_3NO_3$		0.62	ammonia	NH_3		0.10
Isoleucine	ile	$C_6H_{13}NO_2$		131.18	isoprene	C_5H_8		0.97				
Leucine	leu	$C_6H_{13}NO_2$		131.18	isoprene	C_5H_8		0.97				
Lysine	lys	$C_6H_{14}N_2O_2$		146.188	ε-caprolactam	$C_6H_{11}NO$		0.68	ammonia	NH_3		0.12
Methionine	met	$C_5H_{11}NO_2S$		149.21	feed grade methionine	$C_5H_{11}NO_2S$		1				
Phenylalanine	phe	$C_9H_{11}NO_2$		165.19	styrene	C_8H_8		0.63	ammonia	NH_3		0.10
Proline	pro	$C_5H_9NO_2$		115.13	γ-butyrolactam	$C_4H_6O_2$		0.75				
Serine	ser	$C_3H_7NO_3$		105.09	ethylenediamine	$C_2H_8N_2$		0.45				
Threonine	thr	$C_4H_9NO_3$		119.12	isopropanolamine	C_3H_9NO		0.63				
Tryptophan	trp	$C_{11}H_{12}N_2O_2$		204.225	adipic acid	$C_6H_{10}O_4$		0.54	ammonia	NH_3		0.17
Tyrosine	tyr	$C_9H_{11}NO_3$		181.19	styrene	C_8H_8		0.57	ammonia	NH_3		0.09
Valine	val	$C_5H_{11}NO_2$		117.15	isobutyraldehyde	C_4H_8O		0.62	ammonia	NH_3		0.15
General	**AA**	**$C_3H_6O_2N$**		**88.085**	ammonia	NH_3		0.19				

*Isoleucine and leucine while cleaving a ammonia group do not yield a secondary product as it is internally consumed

8

153

Table 9 presents the energy requirements of the solubilization, isolation and purification steps. The final calculated values are functions of these steps, the actual amino acid distribution in the biomass material (Figure 2), the residual protein concentration of the half-product stream, the product conversion yields (Table 8), and the maximum concentration possible to allow for the separation and purification. The calculated values for each biomass feedstock cannot be easily presented, thus Figure 5 is a representation using a set half-product protein (amino acid) content of 6.5 weight percent and depicts an equal amino acid distribution. The total conversion energy required for the "representative" final product ranges between 5 and 35 GJ/ton; with some extremes of up to 200 GJ/ton for highly dilute systems. Illustrated on the secondary vertical axis is the "overall yields" for the 17 products in relation to the initially isolated protein content.

Table 9   Solubilization, Isolation and Purification Operation Process Energy/Exergy Input

Type	Thermal Energy	Electric Energy	Product Relation
Proteases	1.14 – 3.41GJ/ton AA (1.83)	0.33 – 1.97GJ/ton AA (0.39)	2.67/1.49
Nanofiltration	-	1 – 7kWh/m³ (3.5)	0.194 GJ/ton
Electrodialysis	24.2 – 74.8kWh/m³ (33.8)	85.8 – 265.2kWh/m³ (119.7)	8.5 GJ/ton
Chromatography	42.9 – 123.2kWh/m³ (97.5)	12.1 – 34.8kWh/m³ (27.5)	6.9 GJ/ton
Reverse-Phase	36.2 – 37.1kWh/m³ (36.4)	15.2 – 32.3kWh/m³ (19.0)	3.1 GJ/ton
Reverse Osmosis	-	2.5 – 10kWh/m³ (9.0)	0.498 GJ/ton

- value range (brackets chosen): # - # (#)
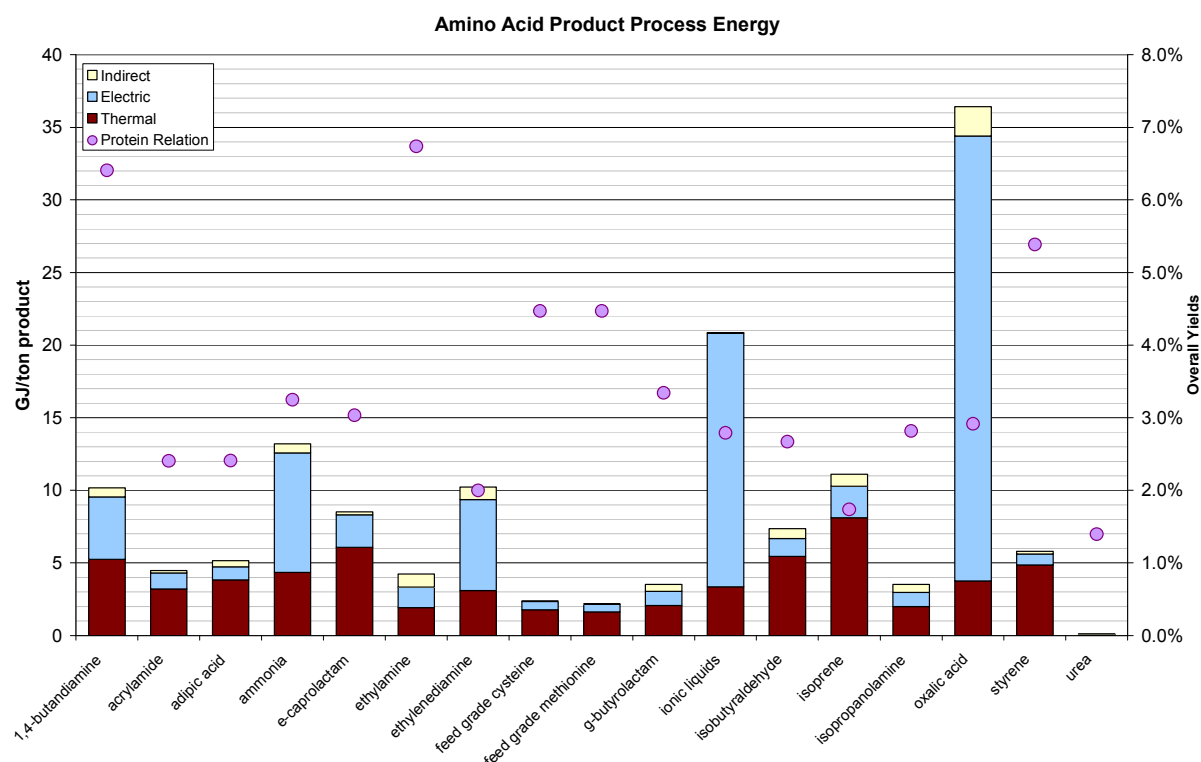

Figure 5   Potential Amino Acid Chemical Product Process Energy
- Portrayal: based on 6.5wt% feed solids loading and equal amino acid distribution

154

8.3.4 *Lignin Processing*

Both soluble and insoluble lignin, along with any residual and unreacted products, are separated together during the amino acid processing stage. Although it is not fully clear how lignin could be used as a commercially viable product, focusing on maintaining and incorporating the aromatic structures is desirable. One option would be to utilize the aromatic backbone for fermentation. Initial studies use waste benzoic acid as feedstock source, but the potential of using lignin in its place was also demonstrated [59]. Another option, incorporated in the matrix, is *fast*-pyrolysis. Initial fast-pyrolysis experiments yielded significantly higher proportional concentrations of simple phenolic structures like phenol, toluene and benzene as opposed to other aromatics[60, 61]. From woody biomass – high lignin content, 52% pure phenol could already be achieved[62]. However, these possible process routes are still largely hypothetical and will require continued research. Table 10 presents an overall estimate of the calculated energy demands focused on the three potential phenolic aromatics.

Table 10 Process Energy/Exergy Input – Lignin to Aromatics

Product	Phenol	Styrene	Toluene
Conversion Rate (%)	18.5	20.5	18.1
Electric Energy (GJ/ton)	0.11	0.12	0.11
Thermal Energy/Exergy (GJ/ton)	3.00/1.44	3.32/1.60	2.94/1.41
Indirect Energy/Exergy (GJ/ton)	-/-	-/-	-/-

8

8.3.5 *Ash Processing*

The gaseous residues of the fast-pyrolysis (lignin processing) stage and the unreacted solid bottoms material are collected and combusted in a combined heat and power plant (CHP). The thermal energy and electric energy will partly offset the internal processing energy costs of the biorefinery. It is however unlikely for most systems that the ash-rich stream will provide enough thermal and electric energy for the entire biorefinery. Furthermore, the high concentration of metals in the ash stream may cause internal combustion problems. Therefore co-firing is a likely solution, with coal being the best candidate. A coal CHP has an output efficiency of 35% electric and 50% thermal energy (30% on basis of exergy). In cases where more electricity is needed then the co-fired coal CHP can provide, electricity is imported from the grid. At the Port of Rotterdam this is implicitly produced via natural gas turbines operating at 45% electric energy efficiency. In cases where more thermal energy is needed it can be imported via a direct coal furnace operating at 85% thermal efficiency (50% exergy).

The metal oxide residues form the remaining ash, which can be used as a soil nutrient replacement. Due to the nature of the high-temperature co-firing combustion, the ash cannot be effectively used in its present state[63]. It can however be placed in a land reclamation (land mass polder) for up to 25 years, which will over time create a perfect soil nutrient replacement and by placing a legume cover crop during the last phase, it may also fix nitrogen[64].

8.4   Results and Discussion

8.4.1   *Overall Biorefinery Fossil Fuel Energy Savings*

Figure 6 (Grass-NL) and Figure 7 (Oil palm-MY) are used to visualize the calculation results in the matrix and like the methodology their construct was explained in earlier work[11]. Noticeable is the heading "next generation", explicitly pointing out the developmental leap from biofuels to dedicated chemical biorefineries. The pictorial representation illustrates the total cumulative fossil fuel energy involved starting from the feedstock and tracing the various process costs to the final array of chemical products from both the traditional petrochemical and biomass production routes. For both fossil and biomass, the straight arrows represent the relative feedstock energy cost and the dotted connecting arrows, the products relative process energy. Presented in the brackets is the total CEC involved in processing the resulting array of chemical products originating from the biomass feedstock route compared to the equivalent naphtha feedstock route. On the biomass products side (left) the boiler output is listed in direct energy terms which was used in the model to offset a portion of the internal processing requirements; this is already taken into account in the final biorefinery cumulative fossil fuel energy value.

Despite being included, net energy value (NEV – the ratio of the output or mitigated energy contained in the products compared to the total invested energy) and (its inverse, in percentage) breeding factor (BF), as argued in previous articles are not sufficient in assessing biorefinery systems[13, 15, 33]. The most important *impact assessment* figures are relative fossil fuel energy savings (relative to e.g. kg biomass or land). Table 11 presents the resulting fossil fuels saving (energetically and exergetically) for the select crops within the calculation matrix. Malaysian palm oil and the Dutch rye grass are two significantly different crops; tropical vs. temperate, oil-rich vs. protein-rich, half-product processing vs. fresh/direct processing, etc. They were intentionally chosen for pictorial representation because, of the selected biorefinery cropping systems, grass has the best energy savings in chemicals terms ($GJ/ton_{chemical}$) while oil palm is best in land savings (GJ/ha). They perfectly illustrate the contrast between generally high yielding crops and those lower yielding crops well suited for chemical biorefineries. It is not surprising that oil palm with its 25.0 ton_{fruits}/ha yield can achieve the highest savings per arable land. Surprisingly however, grass, at only 40% the total biomass yield (14.1 ton_{hay}/ha), achieves 1.4-fold more energy savings per chemicals produced than oil palm (50.8 vs. 37.0GJ/ton). Thus, the overall performance is a combination of yield, biochemical composition and concentration for downstream processing. Figures 6 & 7 highlight this; for example, the relative energy input for the clustered amine chemical products from grass is 12.2 GJ/ton where it is 39.1 GJ/ton from oil palm.
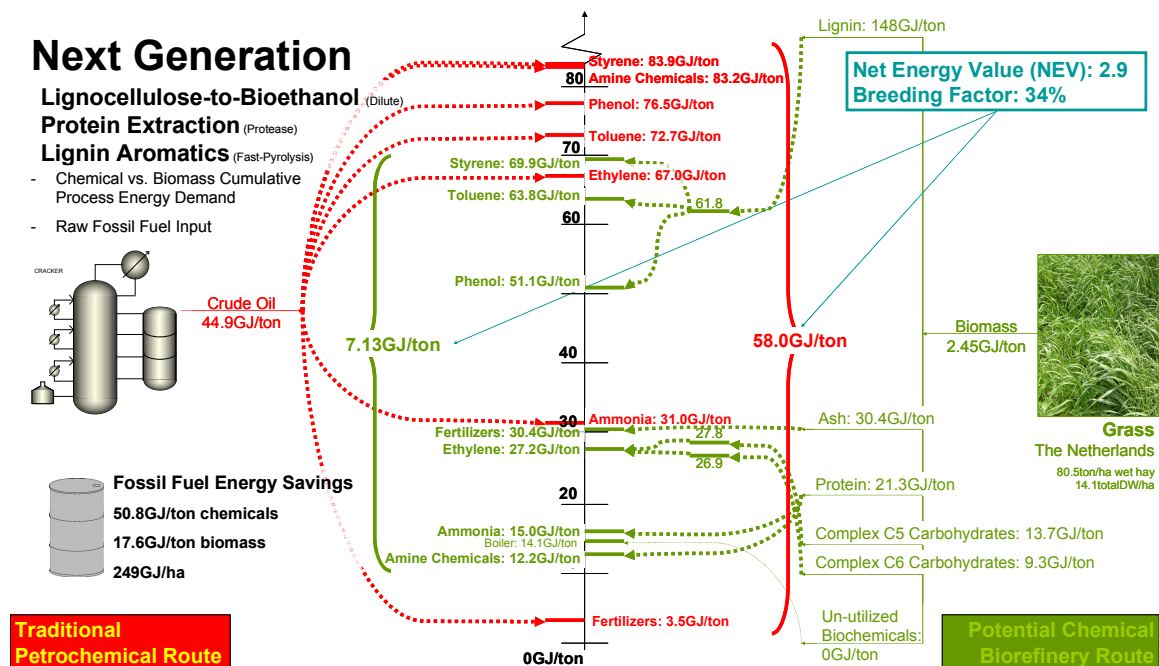
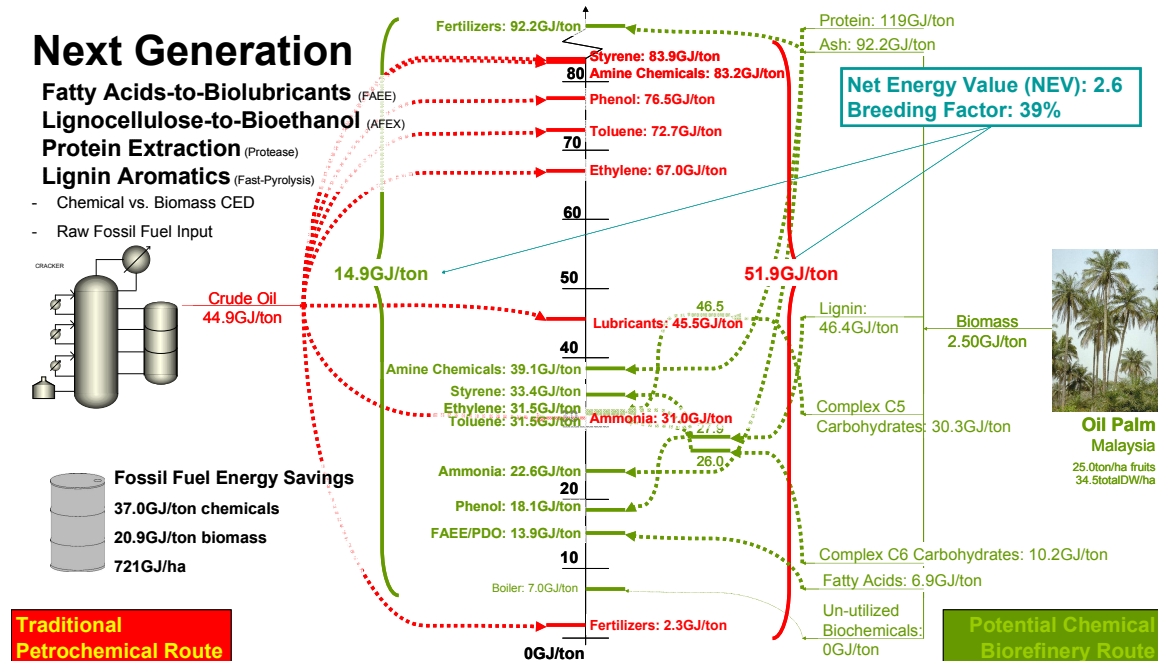Figure 6   Pictorial Representation of Chemical Biorefinery (Grass, NL)

Figure 7   Pictorial Representation of Chemical Biorefinery (Oil Palm, MY)

Table 11　Resulting Overall Fossil Fuels Savings

Crop	Location Region	Fossil Fuel Savings (energy)			Fossil Fuel Savings (exergy)		
		/chemical	/biomass	/ha	/chemical	/biomass	/ha
Cassava	Nigeria	37.1	12.5	438	69.1	23.3	817
Grass	Holland	50.8	17.6	249	55.6	19.3	272
Lucerne	South Dakota	29.2	12.4	186	30.7	13.0	195
Maize	Iowa	45.4	15.4	382	52.6	17.9	444
Oil palm	Malaysia	37.0	20.9	721	42.6	24.0	830
Potato	Holland	34.5	11.4	200	69.8	23.1	405
Rapeseed	Belgium	41.9	21.5	353	44.8	22.9	377
Sorghum	Kenya	39.0	12.3	455	73.0	23.0	851
Soya bean	Illinois	40.3	18.1	196	42.5	19.1	206
Sugar beet	Germany	32.3	10.0	292	67.6	20.9	610
Sugar cane	Brazil	42.0	11.3	490	84.3	22.6	985
Sunflower	France	22.2	15.3	128	22.5	15.5	130
Switchgrass	Iowa	38.5	14.8	208	43.7	16.9	236
Tobacco	Australia	35.5	13.1	346	59.6	21.9	582
Wheat	France	49.6	18.5	343	55.5	20.7	383
Willow tree	Sweden	44.0	15.6	125	50.5	17.9	143

- /chemical: GJ per ton biorefinery chemical mixture
- /biomass: GJ per ton total dry weight harvested biomass processes
- /ha: GJ per arable cultivated land in hectare

8.4.2　Optimal Biorefinery Cropping System

The most important impact assessment terms: savings per produced chemicals (production efficiency) and savings per arable land area (land use efficiency), provide the information necessary to determine the optimal biorefinery cropping system. Their combined results, based on energy savings, are normalised and expressed in a single chart, Figure 8. The biorefinery cropping system option closest to the upper right-hand corner has the best overall performance. Grass with the highest chemical mixture savings is located at the top of the graph but towards the left due to its lower land use efficiency. Oil palm with the best land savings is located at the right of the graph but towards the centre due to its lower production efficiency. Nevertheless, Malaysian oil palm land use efficiency is so high that it still scores as the optimal biorefinery cropping system overall from those assessed.
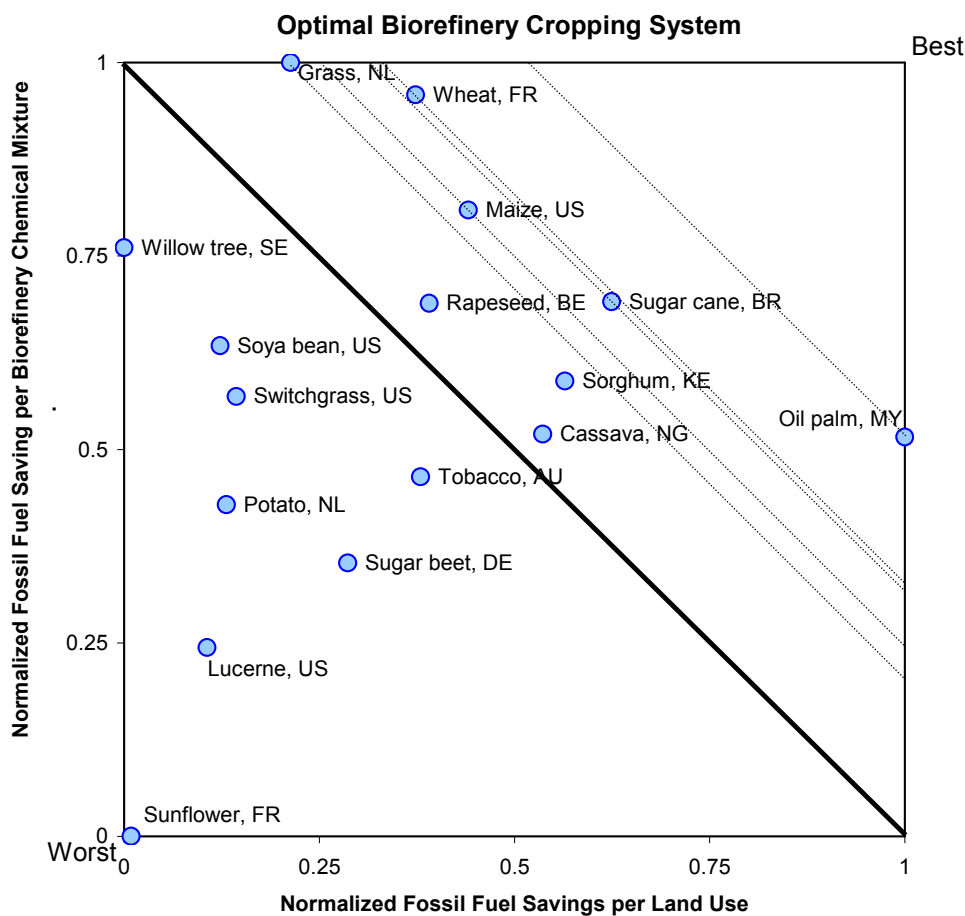
Figure 8 Graphical Determination of Optimal Biorefinery Cropping System

A distinctly different pattern emerges with the plotted exergy values (Figure 9). The previous energy-based savings graph depicts the current situation, i.e. what use **is** made of the resources. The exergy based Figure 9 depicts the thermodynamic situation, i.e. what use **could be** made of the resources. Indicating a possible technologies and integration options for a more efficient use of the current resources (material and energy) following the outlined biorefinery processes. The latter graph is therefore a projection of the potential; the former of the current state-of-the-art. This explains why the exergy-based savings (Table 11) are always noticeably higher than the energy-based savings. The top 5 performing biorefinery cropping systems are listed in Table 12 for both energy and exergy savings. Exergetically, many other crops outperform palm oil: (German grown) sugar beet, (Nigerian grown) cassava, (Kenyan grown) sorghum, with (Brazilian grown) sugar cane as the most optimal in respects to production and land use efficiencies. Oil palm remains a major contender due to it high yields but its position is reduced as biolubricant (biodiesel) processing is mature with only minor foreseeable work efficiency improvements on current technologies. A similar trend is noticed for other oil-based crops, such as soya bean and rapeseed.
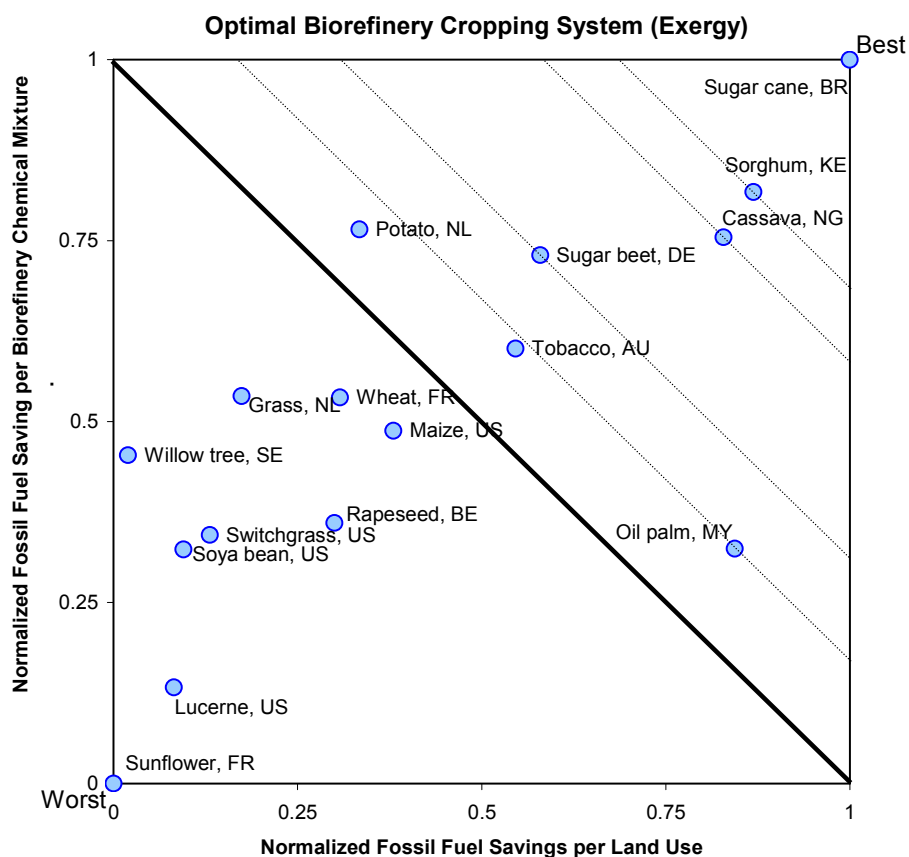
Figure 9   Graphical Determination of Optimal Biorefinery Cropping System (Exergy)

Table 12   Top 5 Cropping and Biorefinery System of Energy and Exergy Fossil Fuel Savings

Top 5 Crop/Biorefinery	Nominal Energy Savings	Nominal Exergy Savings
1	Oil Palm, MY	Sugar Cane, BR
2	Sugar Cane, BR	Sorghum, KE
3	Wheat, FR	Cassava, NG
4	Maize, US	Sugar Beet, DE
5	Grass, NL	Oil Palm, MY

8.4.3   Optimal Combination

In both Figures 8 and 9 the French oil-based crop, sunflower, is consistently indicated as the "worst" performer. The low yield is the primarily factor contributing to the "less good" performance of sunflower but is also attributed to the fact that it is a relatively energy intense crop to cultivate (Table 2). Nevertheless, it still has a replacement potential of 21.9 $GJ_{energy}/ton_{product}$ and 126 GJ_{energy}/ha. This is comparable to, if not slightly better than the current average 1st generation bioethanol production in Brazil, which mitigates 23.5 GJ/ton and 104 GJ/ha following the same methodology[15]. As a result even the "worst" biorefinery cropping system aimed at producing chemicals can compete with the "best" system aimed at producing biofuels.

As a rule of thumb the higher the dry weight yield, the better the crop performance, especially with regards to land use efficiency. Potato (NL) and wheat (FR) both have comparably mid-range yields but are cultivated with a fairly low agricultural intensity in relation to the total dry weight yield. Wheat therefore performed high in the energy savings per chemical mixture and overall as did the potato, albeit on the exergy side. Therefore, even as these are temperate crops, they can approach the overall savings values of their higher yielding tropical counterparts. There are some desirable properties that can steer a cropping system to better performance: high yields with an offset agricultural energy intensity, but also irrigation that is not based on the use of aquifers (as is the case for lucerne-US), low lignin and high protein content (i.e. frequent harvesting & best bioprocessing), low harvestable moisture content, and a location close to a port or waterway.

There is however no single optimal cropping system. Biomass is typically harvested at specific time intervals with an irregular production over the year. Meanwhile it is imperative for the successful forward integration of the large-scale centralized biorefinery to operate like any other production plant within the petrochemical cluster. Therefore, it must be able to process biomass constantly throughout the year. A biorefinery cropping system is therefore only optimal when it has the flexibility to process different feedstock. In this sense, local crops from the hinterland and other temperate crops can make a contribution, especially during periods of unexpected delays or production losses of the more favourable variants.

Genetic modification (GM) of crops might assist in increasing the fossil fuel replacement potential: incremental yield gains will promote a land use efficiency increase and regulating the biochemical composition will promote a production efficiency increase. GM technology might ultimately drive the cropping systems further into the upper-right hand corner of the graphs 8&9 to become "better". The crops deemed suitable for genetic modification and those already partially modified (e.g. soya bean and maize) will have the quickest market entry, while more research time is necessary for the other crops. However, modification often sacrifices the yield of many components for the gain of one, meaning the overall balance may also shift in the wrong direction. Consequently, it remains to be seen whether these new GM-crops do indeed contribute positively.

8.5 Conclusions

In light of the impending problems related to fossil fuels (continued supply, price and pollution) alternative feedstocks based on sustainable criteria are gaining interest and momentum. It is thus of great importance to properly assess the replacement potential of fossil fuels within the energy sectors. Early biomass systems based on combustion or conversion to biofuels are sub-optimal, revealing that the standard thinking towards agricultural products must be reassessed[23, 64]. Applying this rationale to other proposed biobased applications revealed that biomass has the largest fossil fuel replacement potential when employed as an alternative feedstock in the petrochemical industry.

Nevertheless, all biomass and conceptual biorefineries layouts are not equal. The optimal biorefinery cropping system was determined by systematically assessing the entire production chains using a LCA calculation matrix. Trend differences between energetic and exergetic results plus considerations for a continuous supply of feedstock reveal that there is not a single optimum but a combination. Even with a combination these crop-biorefinery systems can outperform the current applications of biomass (e.g. biofuels) implying that dedicated chemical biorefineries represent a developmental leap towards achieving maximum fossil fuel replacement.

8.6   Acknowledgements

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8

Summary and Perspectives

Critical evaluation is required to determine the respective impact of replacing fossil fuels in the broad energy sector with sustainable alternative resources. Since the first oil crisis of 1973, *biomass* has been investigated and partially developed to handle virtually all aspects of the energy sector. As a major foreseeable resource, replacing the entire sector with biomass feedstocks has more recently been termed as the *"biobased economy"*. The focus of biomass applications within the energy sector should be based upon ensuring its most effective use, by exploiting its unique attributes. Critically evaluating biomass over the entire production chain reveals that supplying feedstock for the bulk petrochemical industry has the highest potential in replacing the fossil fuel component within the energy sector.

Life cycle analysis' (LCA) is a tool developed to assess the environmental burdens of different products and process, providing a good indication for sustainable development. However, it is innately prone to discrepancies, being heavily reliant on personal interpretations. Therefore comparing separate studies with their respective findings and results is only possible when the base set of assumptions concur. *Chapter 1* described how utilizing the LCA construct and guidelines formed the basis of the *"energetic and exergetic cradle-to-factory gate analysis"*. This approach is able to narrow-down the assessment to the total cumulative fossil fuel energy (and relative work potential efficiency) usage without dwelling on the subjective environmental factors. Following this methodology, 16 common bioenergy crops in different regions along with various biorefinery configurations were assessed based on concurrent matrix calculation principles facilitating a systematic comparison with negligible discrepancies.

The nature of this study, being energetic with exergetic determination, requires an in-depth understanding of the individual process conditions involved along the chain. *Chapter 2* described how previous assumptions contained in LCI-databases (created for the heavy industries) require re-evaluation for biomass applications. *Chapter 3* took this in-depth approach further to another broader assumption, reasoning that sustainable low-input agricultural practices are not suitable for non-food biomass applications. Considering that, simplified, modern agriculture is the conversion of oil and gas products via soil as a medium into biomass material; maximum overall conversion efficiency is desired over the lowest input.

With regards to efficiency for both biomass propagation and conversion, *Chapter 4* indicated that there is still considerable room for improvement in well-developed systems. Assessed in detail for the Brazilian-sugar cane situation, applying best practice conditions can generate several fold the fossil fuel replacement potential. Although based on the current biofuel (bioethanol) market, it also indicated the potential benefits of transitioning to chemical biorefineries.

Construction and implementation of chemical biorefineries will unlikely be immediate or definitive, but will probably be a natural progression of existing biomass processing plants, like biofuels. Development will likely evolve organically from existing facilities making their existence a prerequisite. *Chapter 5 and 6* investigated the effect of protease treatment on the distiller dried grains (DDG) by-product from bioethanol facilities, in order to cleave the contained protein. As a result the amino acids can (in theory) be separated and isolated for subsequent chemical synthesis to higher-value products. *Chapter 7* placed the experimental results in context, demonstrating the step-wise impact of incorporating biorefinery concepts on the fossil fuel replacement potential. As these and other technologies prove successful they will encroach upon the rest of the processes eventually transforming the facilities into full chemical biorefineries. Most of these technologies are still in the early developmental phase, but with step-wise replacement potential, justification for further research is provided. It also provides an indication of the developmental direction to pursue for biomass.

Fermentative processes dominate the conversion technologies, reflecting by the chemical biorefinery capabilities evolving in parallel with progress made in the field of biotechnology. This does not mean that traditional thermo-chemical reactions will be excluded, for most downstream conversion, isolation, purification and many of the other conversion steps are envisioned to rely on those technologies. Regardless, there are many products and processing options foreseeable from the biorefineries.

Confined to a specific set of possible biochemical products, the synthesis of this dissertation, *Chapter 8,* compiled and analysed the resulting matrix calculations for the various bioenergy crops to determine the *optimal biorefinery cropping system.* In response to the food versus fuel issue, a heavy leaning was placed on land use efficiency in relation to the fossil fuel energy replacement potential. All types of biomass will occupy and thus consume land, but when employed for non-food applications it is imperative to ensure that biomass has the highest impact towards its replacement purposes (i.e. sustainability) per arable land unit: having the least impact on land availability for food production. Although no *single* system was determined as the optimum, all systems, compared to the existing uses of biomass, vastly increased the fossil fuel replacement potential. As long as the biomass is produced efficiently and the chemical functionality in the biomass is upheld as a feedstock source, the system is optimal.

The best application of biomass for the replacement of fossil fuels is the petrochemical industry. This is the most intelligent way to incorporate biomass in a future faced with energy scarcity. Since the fossil fuel-based economy is approaching its eventual decline, the best strategy for biomass to contribute towards the post carbon economy is through the chemical biorefinery. In conclusion, if the right decisions are made today, perhaps there is no need to dwell too much on the future (see preface).

Samenvatting en perspectieven

Kritische evaluatie is noodzakelijk om de impact van duurzame alternatieve grondstoffen als vervanging van fossiele energiebronnen vast te stellen. Sinds de eerste oliecrisis in 1973 is biomassa onderzocht en ontwikkeld om te kunnen worden toegepast in bijna alle aspecten van de energiesector. Als grote bron van duurzame energie in de toekomst, wordt het gebruik van biomassa in de gehele energiesector aangeduid met de term *'bio-based economy'*. Aandacht bij onderzoek naar toepassing van biomassa moet, om een zo efficiënt mogelijke toepassing te garanderen, vooral liggen op het gebruik van de unieke eigenschappen van biomassa. Deze kritische evaluatie van biomassa voor de gehele productieketen, onthult dat het voorzien van de petrochemische sector voor bulkchemicaliën het hoogste potentieel heeft van alle energiesectoren om fossiele grondstoffen te vervangen.

Levenscyclus analyses (LCA) is een methode die ontwikkeld is om de milieubelasting van verschillende producten en processen vast te stellen, dit zorgt voor een goede indicatie van duurzame ontwikkeling. Echter, de methode is ze zwaar afhankelijk van persoonlijke interpretaties en daarom vatbaar voor tegenstellingen. Om deze reden is het vergelijken van verschillende studies, met de eigen bevindingen en resultaten, alleen mogelijk wanneer de basisaannames overeenkomen. *Hoofdstuk 1* beschrijft hoe het toepassen van het LCA opbouw en richtlijnen de basis vormt voor de *'energetic and exergetic cradle-to-factory gate assessment'*. Deze aanpak maakt het mogelijk om in te zoomen op de schattingen van de totale cumulatieve fossiele energie gebruik (en relatieve potentiële arbeidefficiëntie), zonder stil te staan bij subjectieve milieufactoren. Aan de hand van deze methode zijn 16 veel voorkomende bioenergie-gewassen, in verschillende regio's, met verschillende bioraffinage configuraties vergeleken; gebaseerd op eenduidige matrix rekenwijzen, hetgeen een systematische vergelijking mogelijk maakt.

De oorsprong van deze studie (die in essentie een energetische en exergetische systeembeschouwing is) vereist een diepgaand begrip van de individuele proces condities betrokken bij de keten. *Hoofdstuk 2* beschrijft hoe eerdere aannames opgenomen in LCI-databases (opgesteld voor de zware industrie) her-evaluatie vereist voor biomassa-applicaties. *Hoofdstuk 3* brengt deze diepgaande methode verder naar een bredere context, door ervan uit te gaan dat duurzame, low-input landbouw werkwijzen niet passend zijn voor niet-voedsel biomassa toepassingen. Als men de versimpelde visie aanneemt dat moderne landbouw de omzetting is van olie en aardgas producten, via de bodem als een medium, in biomassamateriaal; maximale totale conversie efficiëntie is gewenst boven de laagste input.

Met betrekking tot efficiëntie voor zowel biomassa propageren en conversie, *hoofdstuk 4* geeft aan dat er nog steeds aanzienlijke mogelijkheden zijn voor verbeteringen in goed ontwikkelde systemen. Dit is bepaald in detail voor de Braziliaanse suikerriet situatie. Het toepassen van *'best-practice'* condities kan het potentieel voor vervanging van fossiele brandstof door biomassa fors

vergroten. Alhoewel gebaseerd op de huidige (bioethanol) markt, toont het de potentiële voordelen van de transitie naar chemische bioraffinage.

Het bouwen en implementeren van chemische bioraffinaderijen zal waarschijnlijk niet een enkele grote transitie zijn, maar een natuurlijke progressie van bestaande biomassa verwerkende fabrieken, zoals biobrandstoffen. Ontwikkeling zal naar verwachting evolueren van bestaande faciliteiten, wat het bestaan van deze installaties een voorwaarde maakt. *Hoofdstuk 5 en 6* onderzoekt het effect van protease behandeling van het 'distiller dried grains' (DDG) bijproduct van bioethanol faciliteiten om eiwitten te scheiden. Aminozuren kunnen (in theorie) gescheiden en geïsoleerd worden voor verdere chemische synthese in hogere waarde producten. *Hoofdstuk 7* plaatst de experimentele resultaten in context, aantonend dat de stap-voor-stap impact van het in gebruik nemen van bioraffinage concepten op het fossiele brandstof vervangingspotentieel. Als deze en andere technologieën succesvol blijven maken ze vervanging van bestaande processen mogelijk, zodat uiteindelijk de installaties transformeren in volledige chemische bioraffinaderijen. De meeste technologieën zijn echter nog steeds in de vroege ontwikkelingsfase, maar met de stap-voor-stap vervangingpotentieel rechtvaardigt vervolg onderzoek. Het geeft ook een indicatie van de ontwikkelingrichtingingen die kunnen worden nagestreefd voor biomassa.

Fermentatie processen domineren de conversie technologieën, dit is weerspiegeld in de parallelle ontwikkeling van chemische bioraffinaderijen bekwaamheid en het onderzoeksveld van biotechnologie. Dit betekent niet dat de traditionele thermo-chemische reacties worden uitgesloten, omdat de meeste 'downstream' conversie, afscheiding, zuivering en veel van de andere conversie stappen afhankelijk blijven van deze technologieën. Ongeacht, er zijn veel producten en proces mogelijkheden voorzien van de bioraffinaderijen.

Het synthese van deze dissertatie, *hoofdstuk 8*, heeft de matrix-berekeningen voor verschillende geselecteerd bioenergie gewassen en voor een specifieke groep van mogelijke biochemische producten samengesteld om de optimale bioraffinaderij teeltsysteem te bepalen. In reactie op de *'food-versus-fuel'* kwestie, is een zwaarder accent gelegd op landgebruik efficiëntie in relatie tot de fossiele brandstof energie vervangingpotentieel. Alle typen biomassa zullen land in beslag nemen, maar wanneer deze wordt ingezet voor niet-voedsel toepassingen is het noodzakelijk dat het systeem de grootst mogelijke hoeveelheid fossiele energiebronnen zal vervangen per eenheid landbouwgrond: de minst mogelijke impact van landbeschikbaarheid voor voedselproductie. Alhoewel geen enkel systeem is vastgesteld als optimaal, blijken alle systemen, vergeleken met de bestaande gebruik van biomassa, hebben een sterk toegenomen fossiele brandstof vervangingspotentieel. Wanneer de biomassa efficiënt is geproduceerd en conversie van biomassa in chemische producten zo effectief mogelijk wordt gedaan (door gebruik te maken van de natuurlijke chemische functionaliteit in de biomassa) is het systeem optimaal.

De beste toepassing van biomassa voor de vervanging van fossiele brandstoffen is de petrochemische industrie. Dit is de meest intelligente mogelijkheid om biomassa op te nemen in een toekomst met energieschaarste. Aangezien de *'fossil-fuel economy'* zijn uiteindelijke achteruitgang tegemoet gaat, de beste strategie voor biomassa om bij te dragen aan de *'post-carbon economy'* is door de chemische bioraffinaderij. Concluderend, als de juiste beslissingen vandaag worden gemaakt is er wellicht geen noodzaak om te veel uitweiden over de toekomst (zie *preface*).

Zusammenfassung und Aussichten

Der Austausch fossiler Brennstoffe für die Energieversorgung durch nachhaltige, alternative Ressourcen ist ein Thema mit aktuell großer Bedeutung, das kritischer Untersuchung bedarf. Seit der Ölkrise von 1973 ist *Biomasse* immer wieder als Brennstoffquelle für die Energieerzeugung untersucht und teilweise etabliert worden. Unter dem Titel der *„biobased economy"* bzw. der *Bio-basierten Wirtschaft* wird das Ziel, die gesamte Energieversorgung auf den nachhaltigen Rohstoff Biomasse umzustellen, verfolgt. Hierbei wird jedoch außer Acht gelassen, dass andere regenerative Energiequellen weitaus effektiver zur Energiegewinnung eingesetzt werden können. Biomasse bietet weitaus mehr vielversprechende Verarbeitungsmöglichkeiten: Eine Betrachtung der gesamten Verarbeitungskette zeigt, dass das größte Potenzial Austausch fossiler Rohstoffe durch Biomasse in der Nutzung als Rohstoff zur Herstellung petrochemischer Massenprodukte liegt.

Zur Beurteilung der Nachhaltigkeit einer Entwicklung, eines Produktes oder Prozesses dient die Ökobilanz, ein allerdings stark durch den Ersteller subjektiv geprägtes Hilfsmittel. Ein direkter Vergleich voneinander unabhängiger Ökobilanzen ist somit nur möglich, wenn die zugrunde liegenden Annahmen übereinstimmen. *Kapitel 1* führt aus, welche Grundlagen und Annahmen die Basis der aufgestellten Ökobilanz *„energetic and exergetic cradle-to-factory gate analysis"* bilden. Dieser Ansatz ist auf die Bewertung der möglichen fossiler Brennstoffeinsparung sowie die verhältnismäßig Nutzarbeit fokussiert, ohne dabei auf subjektiv bewertete Umwelteinflüsse einzugehen. Anhand dieser Methode werden 16 verbreitete Bioenergie-Pflanzen, in verschiedenen Regionen angebaut und an verschieden konfigurierte Bioraffinerien gekoppelt, in eine Matrix gestellt und systematisch miteinander verglichen.

Diese Art der Betrachtung – Bestimmung sowohl der Energie als auch der Exergie – erfordert ein genaues Verständnis der Prozessbedingungen eines jeden Verarbeitungsschrittes. *Kapitel 2* widmet sich der Anpassung vorhandener Annahmen aus Ökobilanzinventar-Datenbanken, die für die Schwerindustrie erstellt wurden, für die Nutzung in Biomasse-Anwendungen. Basierend hierauf wird in *Kapitel 3* dargestellt, warum nachhaltige, niedrigarbeitsaufwendiger Landwirtschaft nicht zum Anbau von Biomasse, die nicht für die Verarbeitung zu Lebensmitteln gedacht ist, geeignet ist. Zusammenfassend und vereinfachend gesagt ist das Ziel der modernen

Landwirtschaft ist die Umwandlung von Öl- und Gasprodukten zu Biomasse in der Erde; angestrebt wird hierbei eine Maximierung des Wirkungsgrades bei minimiertem Energieeintrag.

Dass selbst in weit entwickelten Biomasse-Systemen die Effizienz hinsichtlich Transport / Verbreitung / Vermehrung und Umwandlung erheblich gesteigert werden kann zeigt *Kapitel 4*. Anhand des Beispiels „Zuckerrohranbau und –verarbeitung in Brasilien" werden Wege gezeigt, wie ausgehend vom Status quo das fossiler Brennstoffersparnispotenzial durch die Nutzung optimaler Verfahren vervielfacht werden kann. Hier wird auch neben der heutigen Nutzung als Biokraftstoff (Bioethanol) das Potenzial der weiteren Verarbeitungen in Bioraffinerien deutlich.

Es wird nicht davon ausgegangen, dass unmittelbar mit dem Bau der notwendigen chemischen Bioraffinerien begonnen wird. Anzunehmen ist, dass bestehende, Biomasse verarbeitende Anlagen – zum Beispiel zur Herstellung von Biokraftstoffen – evolutionär an die neuen Anforderungen angepasst werden. In *Kapitel 5 und 6* wird die Protease-Behandlung zur Spaltung von Eiweiß in *distiller dried grains (DDG)*, einem Nebenprodukt in der Bioethanolherstellung untersucht. Die so gewonnenen Aminosäuren können theoretisch für die chemische Synthese zu höherwertigen Produkten separiert und isoliert werden. In *Kapitel 7* werden diese experimentellen Ergebnisse auf den industriellen Maßstab projiziert. So wird gezeigt, wie die schrittweise Einführung von Bioraffinerie-Prozessen zu steigendem fossiler Brennstoffersparnispotenzial führt. Jeder vorangegangene, erfolgreiche Schritt eröffnet dabei Möglichkeiten für weiterführende Prozesse, um schließlich vollständige Bioraffinerien entstehen zu lassen. Heute stecken viele der hierfür notwendigen Technologien noch in den Kinderschuhen. Die dargestellte schrittweise Weiterentwicklung schafft sich selbst mit jedem erfolgreichen Schritt die besten Argumente zur Fortsetzung des eingeschlagenen Weges und kann immer wieder auf die verheißungsvollsten neuen Prozesse fokussiert werden.

Fermentation wird die am häufigsten angewandte Art des Umwandlungsprozesses in der Bioraffinerie sein. Fortschritte, die in der Biotechnologie gemacht werden helfen, die Leistungsfähigkeit der Bioraffinerien zu steigern. Selbstverständlich werden klassische thermochemische Reaktionen und Verfahren, insbesondere in weiterverarbeitenden Umwandlungs-, Trennungs- und Reinigungsprozessen, weiterhin eine wichtige Rolle spielen. Sicher ist, dass es in Bioraffinerien eine große Anzahl an Prozessen und Produkten geben wird.

Im Synthese dieser Arbeit, *Kapitel 8*, wird die Matrix möglicher Biomasse-Pflanzen mit dem Ziel, für eine Auswahl biochemischer Produkte das *optimale Bioraffinerie-Getreideanbausystem* zu finden, gelöst. Um dem Aspekt „Energieträger ersetzt Lebensmittel" Rechnung zu tragen wird besonders auf effiziente Landnutzung als Basis des fossiler Brennstoffersparnispotenzial priorisiert. In jedem Fall wird durch den Anbau von Biomasse fruchtbarer Boden genutzt – umso wichtiger ist es dann, dass, wenn dieses Land nicht zur Gewinnung von Lebensmitteln dient, die alternative Nutzung hinsichtlich höchster Nachhaltigkeit optimiert ist. Keines der untersuchten Systeme

kann isoliert betrachtet als die optimaler nutzen von Biomasse, jedes einzelne aber steigert das fossiler Brennstoffersparnispotenzial im Vergleich zum heutigen Stand um ein vielfaches. Das Optimum für die Nutzung von Biomasse wird durch hohe Wirkungsgrade bei Anbau und Ernte der Biomasse, sowie durch Erhalt und Nutzung ihrer chemischen Funktionalität erreicht.

Die petrochemische Industrie birgt das größtmögliche Potenzial zur Austausch fossiler Brennstoffe durch Biomasse und stellt somit deren bestmögliche Anwendung in Zeiten knapper werdender Energieträger dar. Das Zeitalter der fossilen Brennstoffnutzung geht unweigerlich dem Ende entgegen; der Nutzen von Biomasse im Nach-Ölzeitalter *(d.h. post carbon economy)* wird durch die Weiterverarbeitung in Bioraffinerien maximiert werden können. Werden hierfür die richtigen Entscheidungen schon heute getroffen vielleicht muss man nicht viele Gedanken über die Zukunft zu machen (sehen *preface*).

Acknowledgements

I feel obliged to start off by thanking Pieter Bach and Peter Alderliesten from ECN for bringing me in contact with Johan Sanders and by exerting their impressions of my ability to directly arrange the interview, effectively evading the dull application procedure.

Secondly my primary mentor, Johan Sanders. During the early phases of my research our views regarding the biobased economy and other related worldly matters were pretty much polar. But as we developed our knowledge base in this new field together, concessions were made and now our views have reached the point that some actually overlap. In the beginning it was quite hard for me as one needs to get accustomed to his particular sense of humour and mannerisms, while afterwards it become quite rewarding and thought provoking. In the end it became very stimulating especially as our views evolved. He always believed in me and allowed me to pursue my desires, as long as I could coherently justify them; a crate of wine is also a good motivation.

I am the first PhD student Johan ever had and as I did not initially study in an environment which had many of them, left alone we would have gone astray. Luckily my co-promoters, Paul Struik and Remko Boom, had plenty of experience between them and helped the both of us in many practical matters. Throughout my research they both showed me nothing but enthusiasm and encouragement that I was on the right path, an appreciated necessity when isolated at A&F.

Despite having less contact less Hedzer van der Kooi, in the beginning it was great to have had the guidance into the hardcore sciences of chemical engineering and thermodynamics.

I clearly remember my first working day at A&F having lunch at their make-shift eating area thinking to myself "do I want to be here for 4 entire years?". Would doing a PhD prove to be a physiological and not a intellectual challenge? Being the lone PhD student and significantly younger than the surrounding personnel proved tough indeed, but times quickly changed. As the VPPC group grew more students joined, life got better.

Geerten Merkens is the first whom I want to acknowledge. He introduced me to the Wageningen student-society life to the point that other members were surprised that I was yet again present at one of their functions. Plus, during working time, we had some interesting geopolitical conversions, although not entirely unrelated to our respective topics.

Almost everybody who entered my office became an enjoyable encounter. A desktop study can on occasion get boring and tedious; a disruptive break is much welcomed. Age van der Mei replaced Geerten, but we took the discussions further by his generous and practical gift of a laminated world map. We became good friends and while travelling the world together discussed heavily the ramifications of sustainable development. Despite conversing in English, which he claims the European language of unity, he helped me in several Dutch aspects, i.e. my summary.

I should basically thank all the members of our group for the good atmosphere. I especially enjoyed our monthly drink at the "Vlaams" which definitely added a much needed social element to our group discussions; how best discuss science and technology than impaired?

Of those outside our group Joost van Duuren, the über-kakker, was a pleasant addition. During many of the strictly regulated coffee breaks he provided the big-city elitist attitudes so rare in Wageningen. We could easily discuss (or argue) work, money and the corporate model.

I also went abroad for a portion of my research. At MSU I want to thank Bruce Dale for allowing the exchange to go through and so smoothly. Bryan Bals for showing me patience as I familiarised myself with the lab, which was not only foreign because of its location. Julie, Holly, Ben and some other locals made the time fly by. Normally in Northern Europe we poke fun at the South, but at the lab I met Leo Souse from Portugal and we united as EU compatriots, having some good fun of our own.

Leo is a true workaholic and enthusiastically talked about Brazil, so maybe it was no coincidence that my next foreign experience was to be at the workaholic capital of São Paulo. During a conference in D.C., Mirian Zanchetta and I met, she along with Sonia Chapman helped arrange everything. Rony Sato in particular directly helped me work wise sharing many of his industrial stories and culturally entertaining stories. Rony also helped arrange fun as he said "I can handle the day program and Murilo, you can handle the evening program". Special thanks to Murilo, Fernando, Cleo and others for showing me some of best nightlife I have ever experienced; as they say, work hard, party harder.

Outside of Wageningen, I want to thank my friends from before. Particularly Robert Koplin for supplying me with insider info to the developments of German industry and helping me with German when needed. Kieran Morley for providing an insightful and alternative focal point to the global issues. Thankfully their jokes about my current village-like residency were harmless (although maybe self-pity removes the impact). Visiting them and travelling around always made me feel that Wageningen is actually the centre of Europe. By being in other fields of specialty and discussing with them helps keep things in perspective, affectively preventing tunnel-vision syndrome, affecting so-many scientists.

To my mother for her relentless support, positive words of encouragement and unabated believe in my success. To the Smith's for providing a sense of belonging, and especially Geoff for attempting to bring my English up to par. Finally, Margreet for keeping me firmly on the ground.

To all those I've met along the way that in some way affected me, thanks.

Publications

Brehmer, B., Sanders, J. 2008. Methodology description behind implementing an energetic and exergetic cradle-to-gate analysis for valorizing the optimal utilization of biomass. *Int. J. Green Energy*: In press

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° **Working with Endnote**
° **Techniques for Writing and Presenting a Scientific Paper**

Research and Management Skills:

° **Elaboration research set-up, work plan and time schedule of the PhD project**
° **Foreign Research Exchange & Collaboration, BCRL of MSU, USA**

Oral Presentations:

° **SENSE Summer Symposium, 23 June 2006**
   Amsterdam, The Netherlands
° **International Life Cycle Assessment and Management , 6 October 2006**
   Washington D.C., USA
° **International Exergy, Energy and Environment Symposium , 4 July 2007**
   Évora, Portugal
° **International Conference on Renewable Resources and Biorefineries, 5 June 2007**
   Ghent, Belgium
° **International Conference on Renewable Resources & Biorefineries , 3 June 2008**
   Rotterdam, The Netherlands

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Curriculum Vitae

Benjamin Brehmer was born in Vancouver, Canada on the 24th of August 1981. After graduating from Killarney Secondary School in 1999, he moved to Germany to study Process Engineering and Energy Technology at the Applied University of Bremerhaven. An international directed course he would perform two foreign internships and received both the Bachelor and Masters degrees with honours. His Master Thesis was conducted at Energy Research Centre of the Netherlands (ECN) in the field of bioethanol for biochemicals. In September 2004, he joined the research chair "valorisation of plant production chains" of Wageningen UR to work towards a PhD. The topic is the energy and exergy life cycle assessment of producing bulk-chemicals from a biomass origin in comparison to the traditional petrochemical route.