

Design of biorefinery systems for conversion of corn stover into biofuels using a biorefinery engineering framework

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Abstract

Unlocking the potential and value of lignocellulosic residues is an important step in making biorefineries economically and environmentally promising. This calls for a holistic and systematic approach in designing sustainable industrial systems. In this work, a biorefinery systems via biochemical route (acetone-butanol-ethanol or ABE system) and thermochemical route (gasification and mixed alcohols or GMA system) for converting corn stover into biofuels have been designed using a Sustainable Engineering Framework. The framework involves eight main steps: 1) design problem definition, 2) data collection, 3) process synthesis and simulation, 4) process integration, 5) resource recovery from residues, 6) utility system design, 7) economic and environmental modelling and 8) economic value and environmental impact (EVEI) margin analysis for decision making. Consideration of resource recovery from biorefinery waste streams has proven to be the key in making biorefineries self-sustaining and low environmental impacts.. Simultaneous economic and environmental feasibility assessment at the early stage of process design is highly envisaged. The cost of biofuel production in the ABE system has been found to be 49.2 US\$/GJ, and 69.9 US\$/GJ in the GMA system. The greenhouse gas emissions are 46.2 g CO₂-eq/GJ for ABE and 19.0 g CO₂-eq/GJ for GMA, lower than gasoline (85 g CO₂-eq/GJ). The GMA system is not economically compelling though with high environmental benefit, while the ABE system has shown to be both economically and environmentally feasible.

1 **Keywords:** biorefineries, process design, economic and environmental analysis, butanol, ethanol,
2 biofuels

3 **1. Introduction**

4 Concerns over depletion of fossil fuels, climate change and sustainability have driven the exploration of
5 alternative fuel production from renewable sources. Bioethanol currently dominates the market
6 contributing to 65% of the global biofuel production (BP, 2016). Butanol has attracted significant
7 interests as a better biofuel option. Butanol can be used as transportation fuel alone or blended in
8 gasoline at higher ratios (16 vol%) compared to ethanol (10 vol% for E10 ethanol fuel) (Informa
9 Economics, 2013); and it is also a versatile chemical building block (Mascal, 2012). Producing biofuels
10 such as bioethanol and biobutanol from biomass resources is a promising way forward in meeting the
11 sustainability goals of the transport sector.

12 There are two major routes of producing biofuels from biomass, thermochemical (Dutta et al., 2010)
13 and biochemical (Kumar et al., 2012) conversions. An example of thermochemical route involves
14 gasification of biomass into syngas which consists of carbon monoxide and hydrogen, followed by
15 mixed alcohol synthesis (Dutta et al., 2010). Biochemical route involves sugar fermentation such as the
16 ABE (acetone-butanol-ethanol) process which uses bacteria such as *Clostridium acetobutylicum* (Kumar
17 et al., 2012). Starch and sugar from first generation biomass feedstock are currently exploited in the
18 industry, but this has created market distortions in the food sector, and thus should be avoided in future
19 biofuel and biorefinery developments (Tenenbaum, 2008). Alternative feedstock including second
20 generation lignocellulosic biomass such as wheat straw, corn stover and seed husks (Morone and Pandey,
21 2014), food wastes (The Straits Times, 2016), beverage industry residues (Biofuels Digest, 2015) should
22 be promoted and explored. Another challenge faced by biofuel industry is the high feedstock and product
23 purification costs, which can account for up to 70% of production costs (Technavio, 2015). Furthermore,

1 large scale production is needed to meet the demand for transport fuel in the future and to take advantage
2 of economy of scale.

3 The sustainability issues associated with biofuels are also partly due to their current production in linear,
4 single output process systems, which make inefficient use of the feedstock, energy and water inputs. A
5 more systematic approach is needed for engineering solutions through integrative process systems such
6 as biorefineries. A biorefinery is a facility for the sustainable conversion of biomass into multiple
7 products including chemicals, food, animal feed and energy products through integrated, efficient and
8 flexible processing (Sadhukhan et al., 2014). Recent trends in sustainable process design have been able
9 to incorporate sustainability measures into the process design problem through mathematical
10 optimisation (Chen and Grossmann, 2017), insight based methods (Klemeš et al., 2013), decision
11 support frameworks (Sengupta et al., 2015; Azapagic et al., 2016; Serna et al., 2016) and indicators for
12 sustainable design (Ruiz-Mercado et al., 2016). These various methods have also been adapted to
13 biorefineries for their conceptual process design (Kokossis et al., 2015; Ng et al., 2015; Tsakalova et al.,
14 2015; Moncada B et al., 2016; Sacramento-Rivero et al., 2016)). A framework balancing insights and
15 complex mathematical formulations can offer a better appreciation of the decision-making process and
16 the solutions obtained, especially at the conceptual stage if feedstock (e.g. corn stover) and products (e.g.
17 biofuels) are well defined. Furthermore, the framework should incorporate existing methods and process
18 engineering principles so that it can be easily adopted in biorefinery engineering practice. The above
19 methodologies were proposed based on a reductionist/superstructure approach and they have been found
20 to be useful for decision-making for system design from a spectrum of feedstock-conversion-product
21 routes. However, opportunities such as multiple resource recovery within the system boundary have not
22 been substantially captured using these methods. In this work, resource and energy recoveries have been
23 considered of which these aspects have been neglected in the above methodologies mainly due to the
24 complexity of optimisation models when recycling and resource loops are present.

1 In this paper, we present a Sustainable Engineering Framework for biorefinery process design based on
2 an evolutionary approach which adds the layer of resource recovery from biorefinery residual streams
3 to the traditional process integration and utility system design layer. Furthermore, the framework
4 encourages simultaneous economic and environmental feasibility evaluations to aid decision making
5 towards a more sustainable design. The steps for the framework are presented in the following section
6 and has been applied to design biorefinery systems to convert corn stover into biofuels via a biochemical
7 route (acetone-butanol-ethanol or ABE system) or thermochemical route (gasification and mixed
8 alcohols synthesis or GMA system).

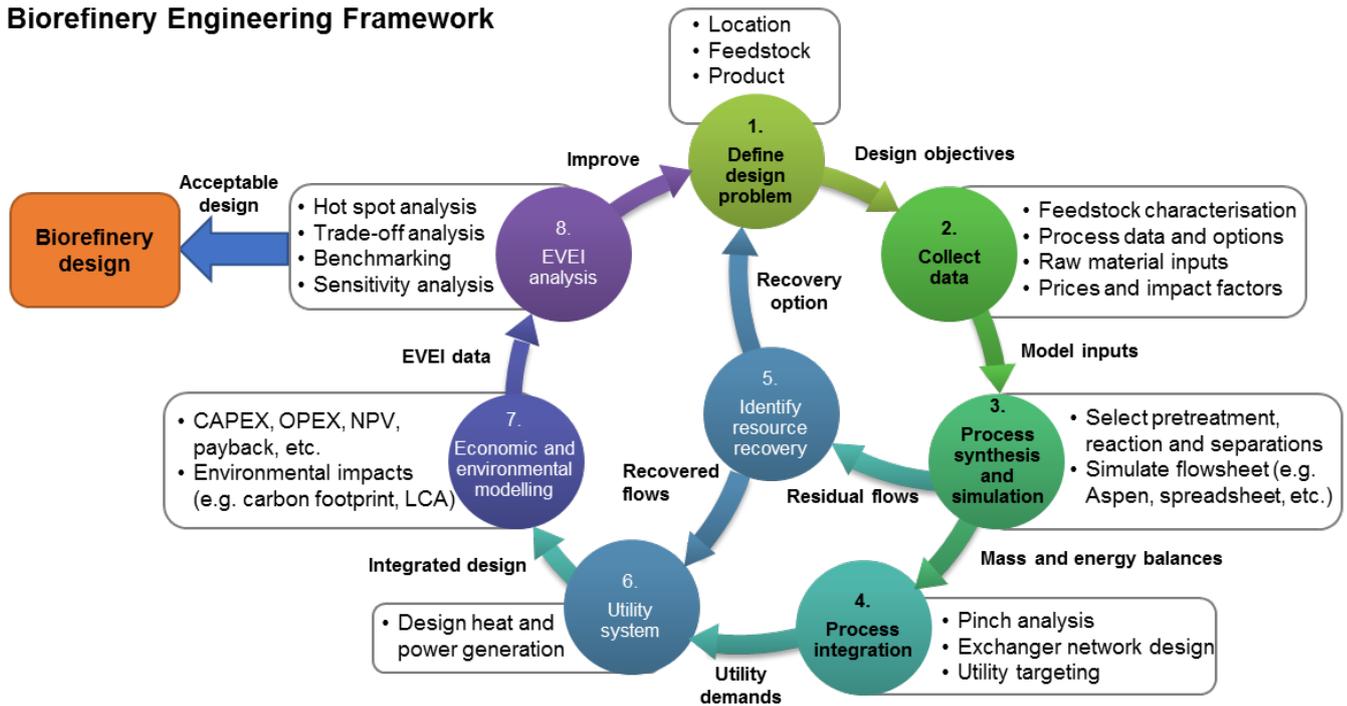
9 **2. Sustainable Engineering Framework for Biorefinery Process Design**

10 The first approach to biorefinery process synthesis and design is the traditional hierarchical procedure
11 by Douglas (1985). A particular aspect of biorefinery design is the presence of three phases, solids,
12 liquid and gas; as well as separations that are mainly used in the specialty chemical production such as
13 centrifugation, filtration, extraction, etc. The presence of water and highly polar organic compounds
14 demands new information of physical properties and models for simulations. Despite the differences,
15 principles from the analogous crude oil refineries can be adopted for designing biorefineries. Crude oil
16 refineries have become efficient thanks to process integration and benefit from self-energy supply by
17 using by-products and residual streams (e.g. off gas, gas oil, etc.). Fractionation of the feedstock into
18 several product lines is another key feature of refineries that can be adopted for biorefineries if
19 lignocellulosic fractions can be separated efficiently. On-site energy and raw material supply can also
20 be achieved through resource recovery from residues and effluents.

21 Capturing the aforementioned process engineering principles into biorefinery design, we present the
22 Biorefinery Engineering Framework (BEF) shown in Figure 1. The eight steps are currently practiced
23 in traditional process design but recovery of materials and energy from biorefinery residual streams can
24 be essential to extract value from every gram in every tonne of biomass and achieve better economic
25 and environmental performance. For this reason, the framework highlights the importance of such

1 resource recovery step during conceptualisation of biorefineries. The eight steps can be grouped into
2 three major tasks of (1) Problem definition, (2) process design and (3) process evaluation. Task 1
3 involves defining the objective of the design (step 1) and gathering the required basic information (step
4 2) required for the later tasks 2 and 3. Task 2 involve process design decisions where process units are
5 selected, a flowsheet is synthesized and process simulation is carried out to determine mass and energy
6 balances in step 3. The information of the process is then passed on to devise process integration
7 opportunities through process-to-process energy integration (step 4) and material resource recovery
8 (step 5). Once process integration allows reducing utility requirements and to know which potential fuels
9 (energy sources) can be recovered and the final demands, the next step is designing the utility system
10 (step 6). While going through these steps in tasks 1 and 3 several options might have been created,
11 therefore task 3 is required for evaluation of alternatives. Task 3 thus involves evaluating the economic
12 and environmental performance through economic and environmental modelling in step 7, so that these
13 criteria can help final decision making of the most promising option or options by analysing trade-offs
14 in step 8. The framework follows a sequential approach but encourages integrated designs and
15 improvement until economic and environmental impact indicators and their trade-offs are acceptable for
16 process engineers and decision makers. Thus, the circular representation highlights the need to iterate
17 certain design alternatives if they are not acceptable and the need to clearly incorporate resource
18 recovery in the design loop. Each of the steps are explained in detail in the following sections.

Biorefinery Engineering Framework



1

2 Figure 1 Biorefinery Engineering Framework for Biorefinery Process Design

3 2.1. Design problem definition

4 In Step 1, the process engineer should clearly define the design problem by indicating the main feedstock
 5 or feedstocks, the desired product and the location. In the framework presented here we assume that
 6 feedstock and main product will be generally defined in the design brief. The plant capacity, operating
 7 hours, system boundary and functional unit for analysis should also be defined here.

8 2.2. Data collection

9 Data collection involves gathering information about a) feedstock characterisation, b) process data and
 10 technology options, c) economic data and d) environmental impact factors. Examples of feedstock
 11 characterisation is shown in Table 1 for corn stover. Process data and options involve information about
 12 chemical reactions, conversion, yields, kinetics and equilibrium, raw material inputs, process conditions,
 13 separation efficiencies and so on. This data may come from literature, experiment or pilot scale trials
 14 and is required for a more realistic process synthesis and simulation. Examples of economic and

- 1 environmental impact data are provided in Table 2, relevant for the processes analysed later. Examples
 2 of reference equipment capital costs are shown in Tables S10 and S13 of the Supplementary Materials.
 3 Table 1 Biomass characterisation of corn stover for biochemical and thermochemical process

Component	% Mass		Component	% Mass
Moisture	20.0		<i>Proximate analysis</i>	
Sucrose	0.6		Moisture	20.0
Extractables	11.7		Volatile matter	60.1
Cellulose	28.0		Fixed carbon	15.4
<i>Hemicellulose fractions:</i>			Ash	4.5
Galactan	1.1		<i>Ultimate analysis</i>	
Mannan	0.5		Carbon (C)	46.86
Xylan	15.6		Hydrogen (H)	5.97
Arabinan	1.9		Oxygen (O)	46.50
Lignin	12.6		Nitrogen (N)	0.65
Acetate	1.4		Sulphur (S)	0.01
Protein	2.5			
Ash	3.9		Heating value (MJ/kg)	16.52

- 4
 5 Table 2 Economic and environmental impact data collected for assessing biochemical corn stover
 6 conversion into biofuels

Item	GHG factor (as CO ₂ -eq)	Unit	Reference	Price ^b (as USD)	Unit

Corn stover	0.095 ^a	kg/kg	Hennecke et al. (2016), Kim et al. (2009)	30	\$/t
Concentrated Acid	0.1	kg/kg	Mu et al. (2010)	275	\$/t
Glucose	0.54	kg/kg	García et al. (2016)	633	\$/t
Ammonia	1.26	kg/kg	Wood and Cowie (2004)	205	\$/t
Corn steep liquor (CSL)	0.5	kg/kg	Mu et al. (2010)	633	\$/t
Nutrients	2.9	kg/kg	Mu et al. (2010)	366	\$/t
Acetone (crude oil based)	2.22	kg/kg	Tao et al. (2014)	1400	\$/t
Ethanol (from corn grain)	2.05	kg/kg	Tao et al. (2014)	502.3	\$/t
Electricity (Mexico mix)	0.173	kg/MJ	Martinez-Hernandez et al. (2014)	0.08	\$/kWh

1 ^a Calculated from carbon footprint for Mexican corn cultivation in Hennecke et al. (2016) and allocated
2 to straw using average ratio from data in Kim et al. (2009).

3 ^b Prices collected from publicly available information online.

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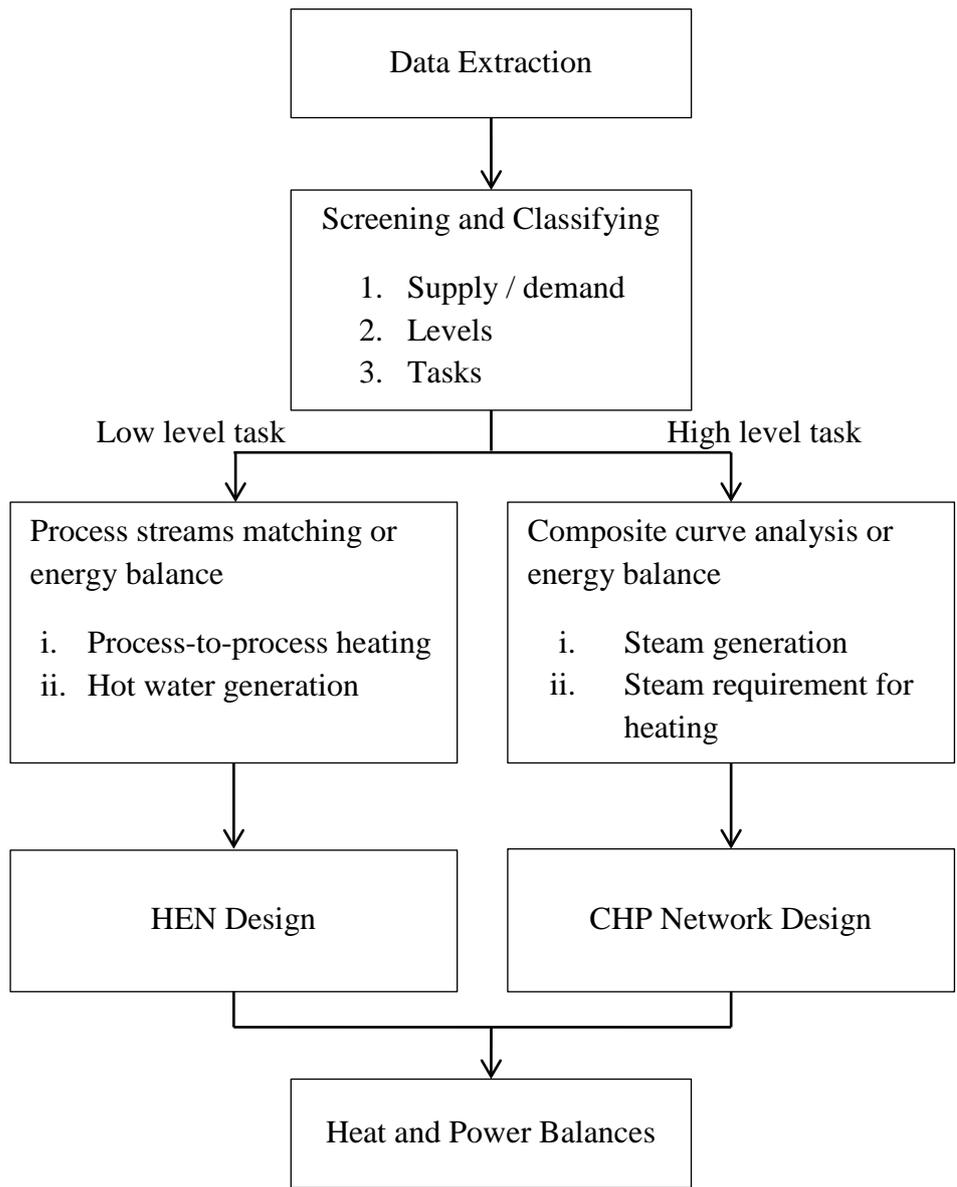
5 **2.3. Process Synthesis and Simulation**

6 The process flowsheet can be synthesised using an evolutionary approach where unit operations are
7 gradually added to create a system structure. In the present study, flowsheets have been simulated using
8 Aspen Plus. The simulation model has been validated against reliable sources, followed by sensitivity
9 analysis on the operating parameters to examine whether the selection of operating conditions has been
10 done appropriately. The process simulation then provides information on the overall product yields,
11 energy requirements and process conditions as well as the flow rates and compositions of residual and
12 waste streams. This information is then used for the next steps of process integration and for
13 identification of resource recovery options.

1 **2.4. Process Integration**

2 Energy efficiency of a biorefinery can be enhanced through systematic energy integration strategies
3 which include data extraction, screening and classification of heat integration task, composite curve
4 analysis, CHP network design and heat and power balance, depicted in Figure 1 (Ng and Sadhukhan,
5 2011; Ng and Sadhukhan, 2011; Sadhukhan et al., 2014). Thermodynamic data such as temperature and
6 heat duty across process units are extracted from flowsheet simulation results. The heat supply and
7 demand of individual units are categorised into high and low level tasks based on the temperature levels
8 and heat duties (Ng et al., 2010). High level tasks refer to steam generation and these are examined using
9 composite curve analysis to estimate the amount of steam that can be generated while energy balance is
10 performed to estimate the amount of steam requirement for heating. The low level tasks consider
11 process-to-process heating and heat utilisation into hot water generation. The strategy considers a high
12 to low level approach, since any excess heat can be used into hot water generation. Process stream
13 matching and energy balance are carried out for analysing low level tasks. The methodology employs
14 pinch analysis for minimum utility targeting and heat exchanger network design based on minimum
15 temperature approach between hot and cold streams. Based on the information obtained from the
16 composite curve and energy balance analyses, heat exchanger network (HEN) and combined heat and
17 power (CHP) system (Section 2.5) can be designed (Sadhukhan et al., 2014; Smith, 2016). The last step
18 is to conduct an overall heat and power balance.

19



1

2 Figure 2: Heat integration and CHP network design strategies (Sadhukhan et al., 2014).

3 Apart from energy integration as shown in Figure 2, pinch analysis can also be used to integrate material
 4 streams. Biorefineries require water especially for cooling, steam generation and for processing (e.g.
 5 fermentation, steam gasification). Water pinch analysis (Wang and Smith, 1994) can be applied to target
 6 recovery and recycling within the biorefinery, thus saving freshwater resource. Another important aspect
 7 is the integration of the various processes in the biorefinery through material streams exchange
 8 (Martinez-Hernandez et al., 2013). Other more advanced process integration and intensification methods
 9 can be applied depending on the scope of the design, such as mass exchanger networks (El-Halwagi and

1 Manousiouthakis, 1989), and hybrid or thermally coupled distillation columns (Caballero and
2 Grossmann, 2013).

3 **2.5. Resource recovery from biorefinery waste streams**

4 In this stage, opportunities for energy, water, nutrient or other resource recovery from residual or waste
5 streams in the biorefineries should be identified. This stage encourages further utilisation of waste
6 fractions and residual streams which allow: a) reducing waste produced by biorefinery processes, b)
7 independence of direct fossil fuel use for biorefinery utilities; and c) improved life cycle environmental
8 performance of biorefineries (Martinez-Hernandez et al., 2014). A systematic way to accomplish the
9 resource recovery step is as follows.

- 10 1. List the utilities or raw materials that the main biorefinery process requires (e.g. electricity, heat,
11 water, nutrients, CO, CO₂, H₂, ethanol, etc.)
- 12 2. Characterise the residual biorefinery stream in terms of physical state (solid, liquid, gas) and
13 properties such as organic content, moisture content, HV, and composition.
- 14 3. As sustainable biorefinery should aim to be energy self-sufficient and minimise the use of fossil
15 fuel, the resource recovery step starts then by identifying options for the use of residual streams to
16 provide energy utilities, then to recover any value-added product and then further conversion into
17 another product. The search for resource recovery options can be accomplished with the following steps:
 - 18 i. Energy recovery. For solids, evaluate their moisture content and heating value, if moisture is low
19 and heating value is significant, then go for combustion and CHP system, alternatively use gasification.
20 If the moisture content is very high consider the liquid stream route. For liquid stream, if organic content
21 is significant, then consider anaerobic digestion for biogas and use biogas for CHP. If the stream is gas,
22 then evaluate its use as fuel for energy generation depending in its composition and heating value. If the

1 residual stream is not a candidate as fuel or substrate for fuel to provide on-site energy utilities then
2 continue to the next step.

3 ii. Material recovery. If the residual stream contains a material used within the process such as a
4 solvent, consider its recovery and recycle. If the residual stream contains a valuable material (e.g. protein,
5 fibre, chemical, etc.), then consider separation and purification and selling as a coproduct. For example,
6 if the liquid stream contains nutrients, consider recovering compost or fertiliser.

7 iii. If the residual stream can be used as a raw material, then analyse its use in a conversion process
8 into value added product such as a platform chemical, a transport fuel, etc.

9 4. List the recovery options identified and form a superstructure. When there are only a few
10 alternatives, a case by case evaluation is practical, however if several complex alternatives are possible
11 then go for an optimisation based approach and formulate the problem. For example, for a given set of
12 main process requirements (energy, water and other raw materials) and a given set of residual streams
13 of composition C_j , find the best combination of resource recovery processes that maximises the
14 satisfaction of the main biorefinery demands and export any excess as a product, subject to
15 compositional, technical, economic and/or environmental constraints.

16 There is also a research opportunity for the process systems engineering community to address the need
17 for methods to simultaneously consider multiple resource recovery in biorefineries.

18 **2.6.Utility system design**

19 Based on the process integration and resource recovery steps, combined heat and power (CHP) plant
20 can be designed once the target for heat utility is set for the biorefinery processes. CHP plant design
21 consists in converting first the energy from available fuels (e.g. char, lignin, biogas) into steam in a
22 boiler. The steam is then used for process heat and the remaining excess steam is used for power

1 generation. This allows for energy self-sufficiency and when there is excess power, electricity can be
2 exported to the grid and can become an important biorefinery income.

3 **2.7. Economic and Environmental modelling**

4 **2.7.1. Economic modelling**

5 Economic analysis forms a critical part of conceptual process design and feasibility study. A
6 comprehensive economic analysis should comprise of capital cost and operating cost evaluations as
7 well as profitability analysis (Sadhukhan et al., 2014). As many of the biorefinery process technologies
8 are yet to be developed at commercial scale, short-cut calculations can be used for a first estimate using
9 correlations and reference capital costs from similar processes, as shown in the following sections.

10 ***Capital Cost***

11 The methodology for capital cost evaluation can be found in Supplementary Materials, Annex A.

12 ***Operating Cost***

13 Operating cost evaluation consists of fixed (maintenance, capital charges, insurance, local taxes,
14 royalties, laboratory costs, supervision and plant overheads) and variable (fuel, feedstock, electricity,
15 catalyst and solvent) costs. Estimation of fixed operating costs can be found in Figure S9 and S12 in
16 Supplementary Materials, while variable operating costs can be obtained from the latest available price
17 data from suppliers' quote.

18 ***Profitability analysis***

19 Profitability analysis evaluates the system economic performance and hence its feasibility.

20 **Total annualised cost** is calculated by summing the annualised capital cost ($C_{capital,annual}$) and operating
21 costs ($C_{operating}$), shown in equation (1).

$$22 \text{ Total annualised cost} = C_{capital,annual} + C_{operating} \quad (1)$$

1 **Economic potential (EP)** is evaluated using equation (2) if values of products, feed, capital cost and
2 operating cost information are available.

$$3 \quad EP = \text{Value of products} - (\text{Value of feed} + \text{Annualised capital cost} + \text{Annual operating cost}) \quad (2)$$

4 **2.7.2. Environmental impact modelling**

5 The environmental impact (EI) generated by a system needs to be assessed to select the process
6 alternatives that have the lowest environmental damage potential. Traditional tools include carbon and
7 water footprint, and the more holistic life cycle assessment (LCA). When LCA is used, various impact
8 categories (e.g. global warming potential, eutrophication, acidification, etc.) should be selected to
9 analyse trade-offs between environmental impacts. The most common categories used in biorefinery
10 design are cumulative primary fossil energy and greenhouse gas emissions (or global warming potential).

11 For a short-cut analysis, the system boundaries can be defined by considering the biorefinery process as
12 the foreground system and the production of all biorefinery inputs as the background system. In this
13 way, instead of doing a detailed life cycle model, factors for the embodied environmental impact of the
14 inputs from cradle-to-biorefinery gate can be used and collected from databases, publications and reports.
15 Then, process simulation will provide information for direct emissions which are then translated into
16 environmental impact (EI). The overall biorefinery environmental impact (EI_{Bioref}) can then be
17 calculated using equation (3).

$$18 \quad EI_{Bioref} = \sum_i^I F_i (EI)_i + \sum_j^J M_j (CF)_j \quad (3)$$

19 where

20 F_i is the flow rate of input i to the biorefinery, e.g. kg/h,

21 $(EI)_i$ is the embodied environmental impact of the biorefinery input i , e.g. kg CO₂-eq/kg,

22 M_j is the flow rate of the direct biorefinery emissions of a given pollutant j , e.g. kg CO₂/h,

1 $(CF)_j$ is the impact characterisation factor of a given pollutant j for a given impact category, e.g. 25 kg
 2 CO₂ equivalents per kg of methane in the 100-year global warming potential impact category.
 3 Another important aspect is the allocation problem that arises when multiple products are obtained from
 4 the biorefinery (e.g. biofuel and electricity). System expansion, where the impacts of co-products as if
 5 generated in a reference system are taken as environmental impact credits, is recommended by the ISO
 6 guidelines. Finally, the net environmental impact of the biorefinery $EI_{Bioref,net}$ is calculated by
 7 subtracting any EI credits due to the co-products as shown in equation (4):

$$8 \quad EI_{Bioref,net} = EI_{Bioref} - \sum_k^K P_k \varepsilon (REI)_k \quad (4)$$

9 where

10 P_k is the flow rate of co-product k , e.g. kg/h,

11 ε is the equivalence factor between the reference product and the biorefinery product, e.g. kg of gasoline
 12 displaced by 1 kg of bioethanol,

13 $(REI)_k$ is the embodied environmental impact of the reference product k , e.g. kg CO₂-eq/kg.

14 Finally, the specific environmental impact for the main biorefinery product is allocated according to the
 15 functional unit chosen for reporting and comparisons (e.g. 1 kg butanol, 1 MJ biofuel energy, etc.),
 16 dividing $EI_{Bioref,net}$ by the relevant flow rate (e.g. kg/h, MJ/hr, etc.).

17 **2.8. EVEI analysis and decision making**

18 Trade-offs between environmental and economic indicators often arise during the analyses, thus to
 19 support decision making, an economic value and environmental impact (EVEI) analysis can be used
 20 (Martinez-Hernandez et al., 2013). The EVEI analysis combines value analysis method for the
 21 evaluation of economic potential with environmental footprinting for impact analysis (Martinez-
 22 Hernandez et al., 2013). Once the energy and mass flows, and the economic and EI costs for each
 23 processing unit are known, a detailed EVEI analysis can be performed for each stream and process

1 pathways to calculate a value on processing (VOP), a cost of production (COP), an EI credit value on
 2 processing (CVP) and EI cost of production (ICP).as described in (Martinez-Hernandez et al., 2013). A
 3 brief description of the methodology is provided in the Supplementary Information. The difference
 4 between VOP and COP is known as economic margin while the difference between CVP and ICP is
 5 known as environmental margin. Environmental margin is the net environmental impact avoidance
 6 assuming replacement or substitution of a reference product.

7 Depending on the phase of design development, a high-level analysis or a unit by unit analysis can be
 8 performed. Assuming that we applied the framework to early stages of developing a biorefinery design,
 9 a high-level analysis is illustrated in the present publication. A plot of total annual economic cost and
 10 value versus the total environmental cost and product displacement credit is generated. The
 11 environmental credit value (EICV) is calculated from the EI of a reference product and the equivalency
 12 factor between the main biorefinery product and a reference product, as shown in equation (5).

$$13 \quad EICV = \varepsilon(REI)_k \quad (5)$$

14 For example, the mass equivalency between butanol and gasoline can be calculated from the heating
 15 value of butanol (33.1 MJ/kg) divided by the heating value of gasoline (44.5 MJ/kg) to get equivalency
 16 of $\varepsilon = 0.74$ kg gasoline/ kg butanol. Using gasoline as the reference and with an EI of 3.8 kg CO₂-eq/kg
 17 gasoline, the EICV of butanol is: $0.74 \times 3.8 = 2.82$ kg CO₂-eq/kg butanol. This can be used to calculate
 18 the total EICV by multiplying with the flow rate or converted into another basis such as per GJ of energy.
 19 An EVEI plot can be constructed as shown in Figure 3a by plotting i) a *value line* which is a plot of total
 20 EI credit vs. total revenue from products, and ii) a *costs line* which is a plot of total EI incurred by the
 21 biorefinery vs. total economic costs of production. The horizontal difference between the end points of
 22 the two lines represents the *economic margin* (Δe) from all the biorefinery products p :

$$23 \quad \Delta e = \sum_p^P (VOP_p - COP_p) \quad (6)$$

1 The vertical difference between the two lines represents the *EI margin* (Δi) of the biorefinery:

$$2 \quad \Delta i = \sum_p^P (CVP_p - ICP_p) \quad (7)$$

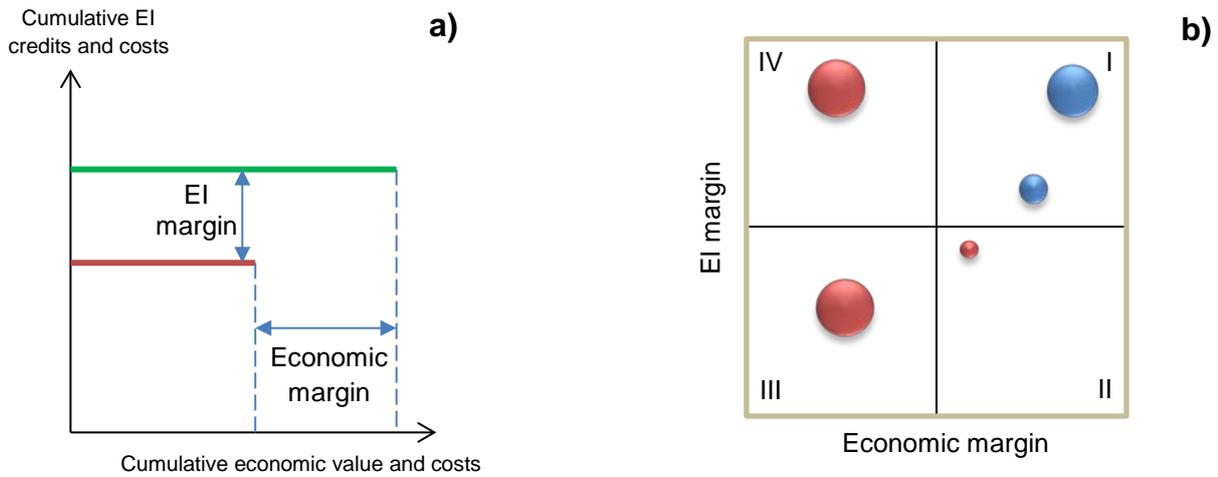
3 A large positive EI margin means the design is environmentally feasible as the EI of the biorefinery
4 system is lower than that of the reference system producing the displaced product. A large positive
5 economic margin shows the design is economically feasible. The EVEI plot therefore shows whether
6 the biorefinery is feasible in terms of both economic and environmental impact. Note that at overall
7 process system level $\Delta e = EP$ and $\Delta i = EI_{Bioref,net}$.

8 Once the margins are known, several indicators can be calculated to support decision making and
9 ranking of design alternatives. For example, the EI margin divided by the economic margin represent
10 the environmental impact avoidance per amount of economic profit (r):

$$11 \quad r = \frac{\Delta i}{\Delta e} \quad (8)$$

12 Trade-offs between the economic objective of maximising profit and the environmental objective of
13 maximising environmental benefit can be visualised better by plotting EI margin vs economic margin
14 of the various process alternatives, as shown in Figure 3b. The bubbles near the x-axis (far from the
15 origin) will indicate small absolute values of r , while bubbles near the y-axis (far from the origin) will
16 indicate large absolute values of r . Therefore, the position indicates the magnitude of r . In this plot,
17 the size of the bubble can be related to a third indicator value, e.g. the energy efficiency of the process.

1 The use of the plots and EVEI analysis is further illustrated in the next section.



2

3 Figure 3 a) EVEI plot of biorefinery showing environmental impact (EI) and economic margins, and
4 b) EVEI margins analysis comparing alternatives with I) economic and environmentally feasible
5 region, II) economically feasible but with unbalanced EI, III) Non feasible region, IV)
6 environmentally feasible but not profitable.

7 **3. Application to corn stover conversion into biofuels via biochemical and thermochemical** 8 **routes.**

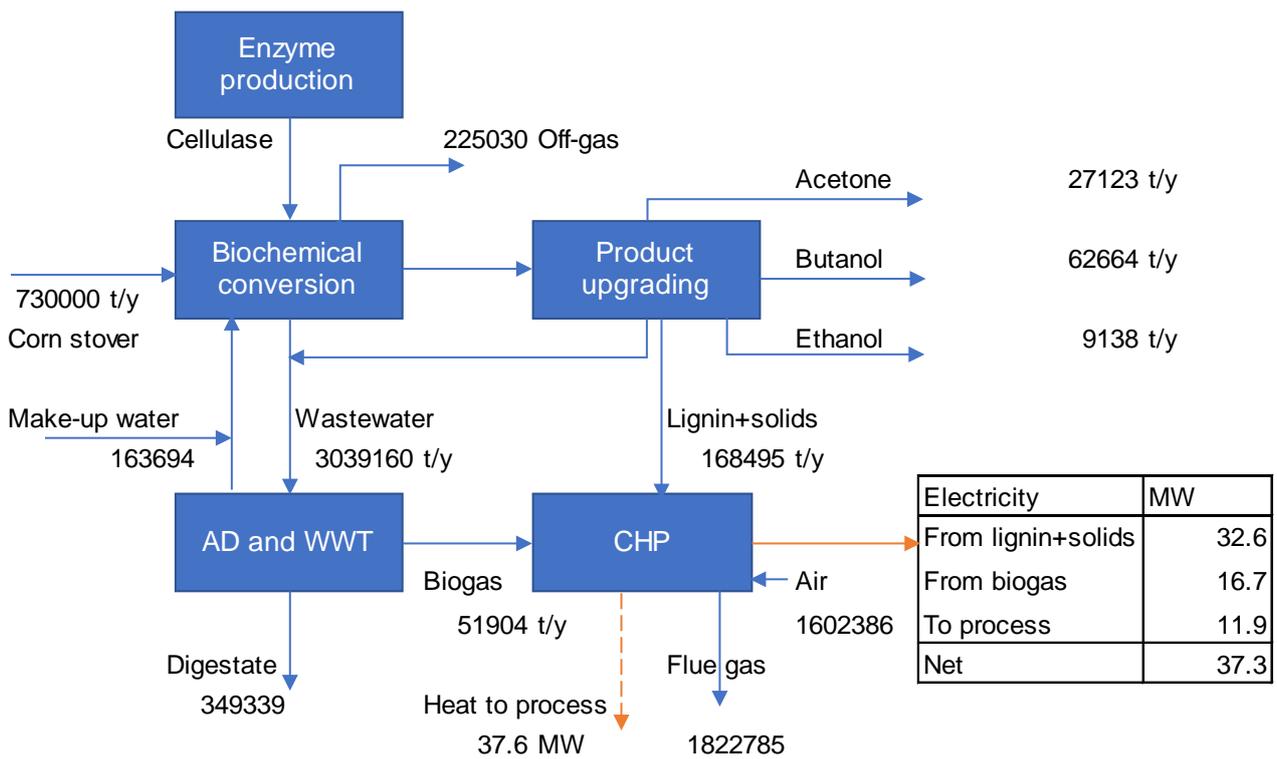
9 **3.1. Design problem definition**

10 The Sustainable Engineering Framework presented in this paper was applied to design two processes
11 for the conversion of lignocellulosic biomass into biofuels via 1) biochemical conversion using the
12 acetone-butanol-ethanol fermentation process, named **ABE** from now on, and 2) via thermochemical
13 conversion using biomass gasification and syngas conversion into mixed alcohols, named **GMA** from
14 now on. An overview of the systems analysed is shown in Figure 4 and 5. The comparison was made in
15 terms of the functional unit of 1 GJ of energy in the biofuel products. Butanol and ethanol in the ABE
16 process, and mixed alcohols in the GMA process, were considered as the main biofuel products. The
17 biorefinery is to be located in a rural area in Mexico and uses corn stover as biomass feedstock with a

1 processing capacity of 730 kt/y of wet corn stover and operates 80% of the year (7008 h/y). The capacity
 2 was assumed to be within the limits of the availability of feedstock closer to the biorefinery plants.

3 3.2. Data collection

4 Data for the corn stover lignocellulosic composition as well as proximate and ultimate analyses are
 5 presented in Table 1. Economic and environmental impact data collected are shown in Table 2. Data
 6 was mainly collected from literature and reports. An effort has been made to use data inventories
 7 applicable for Mexican conditions, however some other data was taken from average values reported in
 8 the literature. This will create some uncertainties but evaluating these was out of scope of this work as
 9 the main purpose was to illustrate the framework in the case study.



10

11 Figure 4 Overview of the biorefinery using corn stover to produce biofuels via the acetone-butanol-
 12 ethanol (ABE) process. CHP: Combined heat and power plant; AD: Anaerobic digestion; WWT:
 13 Wastewater treatment plant.

14 3.3. Process synthesis and simulation

1 **3.3.1. ABE process**

2 This process consists of biomass handling to reduce biomass size, pre-treatment to separate cellulose,
3 hydrolysis to release sugars, and fermentation of sugars into acetone, butanol and ethanol. The
4 fermentation broth then goes to the product upgrading section. The process also considers on-site
5 enzyme production. The synthesis of the ABE process was performed by adapting the process for
6 ethanol production from lignocellulosic biomass presented by NREL (Humbird et al., 2011) as most of
7 the processing units are the same in both processes. The changes made involved changing the set of
8 reactions from ethanol to butanol, acetone and ethanol production in the stoichiometric fermentation
9 reactor models. This also facilitated the simulation of the process by using their Aspen Plus model in
10 which a yield reactor for the ABE fermenters was used. The mass yield of fermenter outlet product per
11 amount of sugars fed to the fermenter was specified as: acetone (9%), butanol (18%), ethanol (3%),
12 acetic acid (1.5%), butyric acid (1.5%), Hydrogen (1.6%), Microbial cell biomass (12.7%), CO₂ (49.7%)
13 and unconverted sugars (3%). The NREL model assumed a continuous operation. The separation and
14 upgrading process was changed completely from the NREL model, as the ABE process requires other
15 separation units.

16 The product separation and purification flowsheet simulated in the present work can be found in Figure
17 S2 of the Supplementary Materials. Our own simulation results give the mass flows shown in Figure 4,
18 with an overall process yield of 3.7% acetone, 8.6% butanol and 1.3 % ethanol with mass purities of
19 99.6% acetone, 99.5% butanol and 99.5% ethanol. Ethanol is dehydrated using a molecular sieve unit
20 (simulated using simple split fractions in spreadsheet). The heating duty for the biochemical and enzyme
21 production conversion sections was 9 MW. The utility needs for the non-integrated product upgrading
22 section were 31.7 MW of cooling duty and 33.2 MW of heating duty. A solvent make-up (n-decane
23 mainly) of 2% from the initial input was required. 3.18 kg water per kg corn stover were also required
24 if recycling is not considered. The total electricity requirement was 11.95 MW. Complete simulation
25 results for mass and energy balance are presented in Table S1 of the Supplementary Materials.

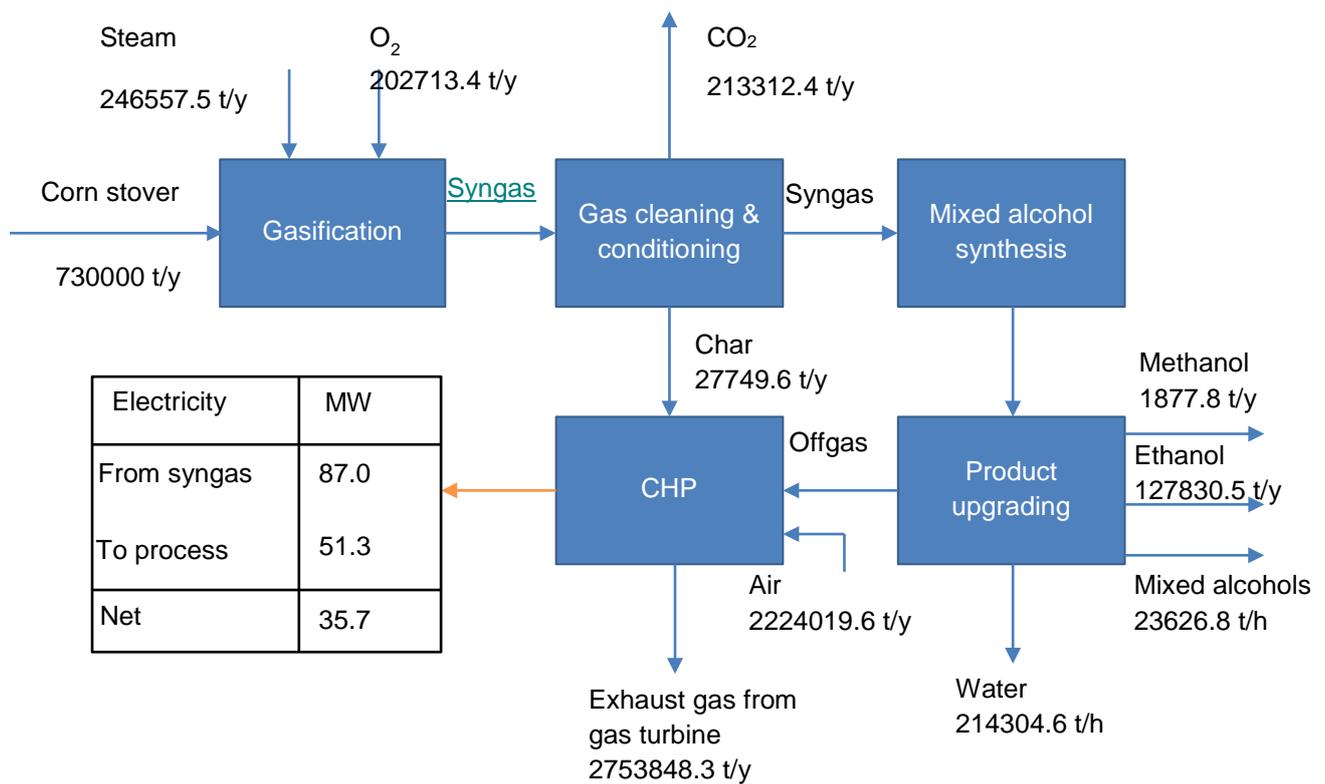
1 3.3.2. Biomass gasification and mixed alcohol (GMA) process

2 In this thermochemical process, biomass is gasified into syngas followed by mixed alcohol synthesis
3 (Phillips, 2007; Dutta et al., 2010). Mixed alcohol synthesis (Equation (9)) operates at temperature of
4 300°C and pressure of 70-150 bar with H₂/CO ratio of the syngas feed of 1.0-1.2 (Phillips, 2007). The
5 products are methanol (5.01 wt%), ethanol (70.66 wt%), propanol (10.07 wt%), butanol (1.25 wt%) and
6 others (Phillips, 2007). A range of heterogenous catalyst can be used, however there is variation with
7 respect to the selectivity of alcohol produced (Gerber et al., 2007).



9 The flowsheet can be divided into four main sections: gasification, syngas cleaning and conditioning,
10 mixed alcohol synthesis and separation, and power generation. The process then was simulated also
11 using ASPEN Plus and the simulated flowsheet can be found in Figure S4 of the Supplementary
12 Materials. Biomass gasification reactions are assumed to be taken place in an interconnected fluidised
13 bed reactor consisting of a steam gasifier and a char combustor. The reactions are modelled using Gibbs
14 reactor (RGibbs) in ASPEN Plus. Volatile gas, tar and char are the main representation of biomass
15 components. Volatile gas (assuming H₂, CH₄, C₂H₆, CO, CO₂, H₂O, N₂ and H₂S) and tar (assuming
16 C₆H₆O, H₂O and O₂) are reacted in the gasifier while char (assuming carbon element only) is combusted
17 to produce energy. The reactions are carried out at 1200°C and 30 bar, with steam input to the gasifier
18 of 0.34 kg/kg wet biomass and oxygen input to the char reactor of 0.3 kg/kg dry biomass, respectively
19 (Tijmensen, 2000). The products from gasification have been validated and the details of the model can
20 be found in the previous published literature (Sadhukhan et al., 2009). Process descriptions are detailed
21 in Supplementary Materials: Annex 2.

22 Simulation results give the mass flows shown in Figure 5, with an overall process yield of 0.3% methanol,
23 17.5% ethanol and 3.1% mixed alcohols. Complete simulation results for mass and energy balance are
24 presented in Table S8 of the Supplementary Materials.



1

2 Figure 5 Overview of the biorefinery using corn stover to produce biofuels via gasification and mixed
 3 alcohol process. CHP: Combined heat and power plant.

4 **3.4.Process integration**

5 Energy integration was performed using pinch analysis for minimum utility targeting and heat exchanger
 6 network design. The composite curves are shown in Figure S3 of the Supplementary Materials. In the
 7 ABE process, the scope for integration was mainly in the separation section as fermentation occurs at
 8 low temperature (35 °C). Three feasible matches were considered, which allowed reducing the cooling
 9 utility by 8.3% to a value of 29.1 MW, and the heating duty by 14% to a value of 28.5 MW, in respect
 10 to the non-integrated upgrading section. This could be further reduced if optimisation and hybrid column
 11 configurations are explored in a more detailed engineering study. The recovered solvent is of enough
 12 purity to be recycled and effluents are sent to the wastewater treatment plant for resource recovery. In

1 the GMA process there was better scope for energy recovery in the form of steam in a heat recovery
2 steam generator (HRSG) as described in section 3.3.2 and 3.6.

3 **3.5. Resource recovery**

4 In the ABE process, several resource recovery opportunities were identified. Wastewater contained
5 around 7% of organic matter while unconverted solids and lignin (lignin + solids) was rich in carbon
6 with a heating value of 20 MJ/kg. Using this information and mass balance results (Figure 4), the design
7 process cycle in Figure 1 was started for the resource recovery from these residual streams. The resulting
8 process consists of anaerobic digestion to recover biogas and nutrients in digestate. The process also
9 allowed recycling 93% of the freshwater required by the main ABE process. Lignin + solids and biogas
10 are then sent to the utility system. In the GMA process, the resource recovered was char which was then
11 used to produce steam and more electricity in the utility system. The gaseous stream from the flash is
12 mixed with other separated gas streams and then compressed to 14 bar and sent to gas turbine for power
13 generation.

14 **3.6. Utility system design**

15 In the ABE process, a CHP plant was designed where lignin + char and biogas were combusted in a
16 boiler (80% efficiency) to generate steam. Steam was used to provide heat utility to the main process,
17 and any excess steam was converted into electricity using steam turbines (at 47% efficiency). Steam
18 generated from lignin+solids was enough to meet the heating demands by the main process and there
19 was excess steam from lignin+solids and all steam from biogas was converted into electricity. The
20 resulting electricity generation and net export is shown in Figure 4. In the GMA process, the CHP plant
21 consists of: (1) expanding the offgas resulting from mixed alcohol synthesis in gas turbine for electricity
22 generation; (2) expanding superheated steam generated from syngas cooler (cooling of product gas from
23 gasification) through steam turbine; and (3) expanding superheated steam generated from HRSG

1 (cooling of gas turbine exhaust) through steam turbine. The electricity production from each biorefinery
2 system and the net excess exported to the grid is shown in Figures 4 and 5.

3

4 **3.7. Economic and environmental modelling results**

5 The economic and environmental modelling results were analysed for a functional unit of 1 GJ of biofuel
6 products. Mass flow rates were multiplied with the respective heating values to obtain the biofuel energy.
7 In the ABE process butanol and ethanol are considered as the biofuel products, and all the alcohols are
8 considered as biofuels in the GMA process. For each tonne of wet corn stover, 3.17 GJ of biofuel energy
9 was obtained in the ABE biorefinery process and 5.0 GJ in the GMA biorefinery process. Both integrated
10 biorefinery systems also export similar amounts of excess electricity of about 0.05 kW/t corn stover.
11 Thus, from an energy yield perspective, the GMA seems to be more advantageous than the ABE process.
12 However, an economic and environmental analysis will support a holistic decision making, as shown in
13 the next sections.

14 **3.7.1. Total annual cost of production and economic potential**

15 Annual capital costs and annual operating costs for the ABE and GMA biorefineries have been evaluated
16 using the methodologies outlined in Section 2.7. The detailed assumptions and results for these two case
17 studies are presented in Tables S10 to S16 of the Supplementary Materials. Discounted cash flow
18 analysis has been conducted for plant life of 15 years and discount rate of 10%, implying an annual
19 capital charge of 13.1%. A comparison of economic performance of ABE and gasification using corn
20 stover as the feedstock is presented in Table 3.

21 Table 3 Summary of economic analysis of ABE and gasification systems for bio-butanol production.

Design specification	
Feedstock	Corn stover

Capacity (t/h biomass input)	104.17	
Operating hours per year (h)	7008	
Result summary		
Technology	ABE	Gasification
Annual capital cost (million USD/y)	49.62	209.24
Annual operating cost (million USD/y)	64.30	45.88
Total annual cost (million USD/y)	113.92	255.12
Total annual cost per unit feedstock (USD/t)	156.05	349.47
<i>Product Value</i>		
Methanol (million USD/y)	0	0.72
Acetone (million USD/y)	38.26	0.00
Ethanol (million USD /y)	4.58	64.20
Mixed alcohol (million USD/y)	0.00	45.53
Butanol (million USD /y)	127.14	0.00
Total (million USD/y)	169.98	110.46
Electricity (million USD/y)	20.90	20.03
Economic potential (million USD/y)	76.97	-124.64

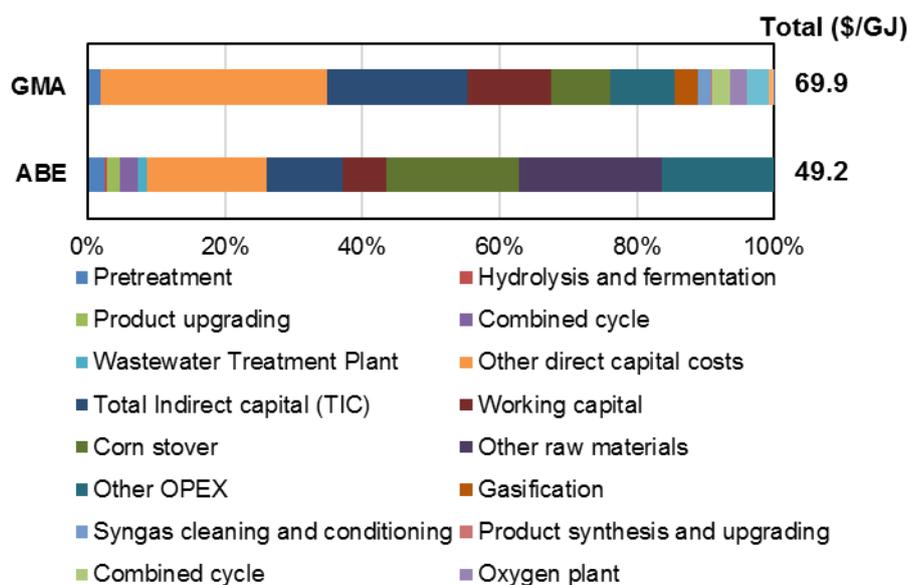
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2 The annual cost for GMA biorefinery system is 4 times of ABE system. This is mainly due to the high
3 capital investment required for high temperature processes such as gasifer, gas compressors and
4 expanders, CHP systems and CO₂ capture facilities. The values of products are in the order of
5 butanol/mixed alcohols (2038.5 USD/t) > Acetone (1400 USD/t) > Ethanol (502.28 USD/t) > Methanol
6 (386 USD/t). ABE has demonstrated a higher yield of higher value products, i.e. butanol (63.3%) and
7 acetone (27.4%) compared to gasification which has ethanol (84.1%) as the main product. Electricity
8 has been generated as side products from the CHP systems and it is comparable in both cases. This can

1 be explained with the values from Figure 4 for ABE process and Figure 5 for GMA process. In ABE,
2 the electricity produced comes from lignin+solids (32.6 MW) and biogas (16.7 MW) for a total of 49.3
3 MW and the consumption by the process is only 11.9 MW which gives a net of 37.3 MW. In the GMA
4 process the total production only comes from syngas and is 87 MW, higher than the ABE process.
5 However, as the system is using an air separation unit, this consumes considerable amount of electricity.
6 The total consumption in GMA process is 51.3 MW, thus in the end it coincided that the net electricity
7 is similar. In summary, the production is higher in GMA than ABE, but GMA consumes higher amounts
8 as well.

9 It is obvious that the economic potential of the ABE system is more promising than GMA system. The
10 economic performance of the gasification case can be improved if the yield can be shifted towards higher
11 amount of mixed alcohols production. In the current analysis, the economy of scale factor has not been
12 considered and this may have an influence on the choices if larger scale of the systems were considered.

13 Figure 6 shows the cost breakdown per GJ of biofuel produced. As observed, the total cost is lower for
14 ABE process and the costs are mainly contributed by operating costs more than the annual capital costs.
15 Major costs are contributed by corn stover and other raw material inputs, other OPEX and indirect capital
16 costs. In the case of GMA, the major costs come from the capital costs as discussed before.



1

2 Figure 6 Cost breakdown per GJ of biofuel produced in two biorefinery systems using corn stover.

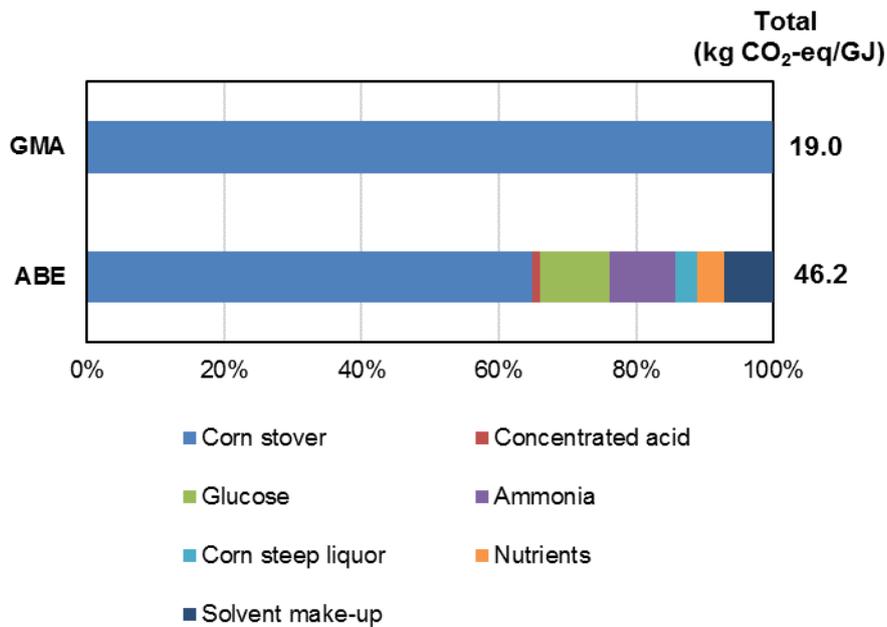
3 ABE (Acetone-butanol-Ethanol) process and GMA (gasification and mixed alcohols) process.

4 3.7.2. Environmental impact

5 A preliminary environmental impact estimation was carried out using life cycle greenhouse gas factors
6 for the biorefinery inputs (Table 2) and using the equations in section 2.7. The functional unit is 1 GJ of
7 biofuel product and system expansion approach was adopted for the co-products. The direct process
8 emissions were also quantified from the simulation results but are not considered as impact from the
9 biorefinery as they are from biogenic origin, i.e. originally captured by corn growth. The EI results are
10 summarised in Table 4 presenting the annual EI incurred from biorefinery inputs (A), direct process
11 emissions (B) as well as the EI credits of the coproducts (D y E) due to displacement of fossil-based
12 equivalent products. The values in the table are allocated to the total energy in the products by dividing
13 by value C in Table 4. Both processes generated similar direct process emissions per GJ (B/C in Table
14 4) of 264 g CO₂-eq/GJ for the ABE process (mainly from fermentation and combustion of lignin+solids
15 and biogas) and 265 g CO₂-eq/GJ for the GMA process (mainly from combustion of char and off-gas
16 and CO₂ separated from the syngas). If only the embodied emissions in the inputs to the biorefinery are

1 considered (A/C in Table 4), the EI per GJ of biofuel were 46.2 g CO₂-eq/GJ for ABE process and 19.0
2 g CO₂-eq/GJ for GMA process, which are already lower than the reference value for gasoline of 85 g
3 CO₂-eq/GJ. Therefore, Table 4 shows the EI credits potential (or the potentially avoided impact due to
4 displacement of gasoline) with and without co-product credits. These values also consider that process
5 emissions are balanced off by plant growth. Figure 7 shows the EI breakdown per GJ of biofuel produced.
6 In this case GMA outperforms ABE biorefinery system mainly because more biofuel products are
7 obtained and less inputs are required for the process. In both systems, the impact from corn stover
8 represent the major contribution. Nutrient supply, solvent make-up and glucose for enzyme production
9 are also major contributors in the ABE case.

10 When the system expansion is applied to account for the co-product credits, the systems achieve negative
11 emissions due to displacement of fossil-based acetone and grid electricity in the ABE process (net
12 emissions of -50.2 g CO₂-eq/GJ), and grid electricity only in the GMA process (net emissions of -23.8
13 g CO₂-eq/GJ). Although both systems displace similar amount of electricity, the ABE system shows
14 better due to additional avoidance by displacement of fossil-based acetone. However, this is reverted
15 when the CO₂ captured in the GMA process is considered, resulting in -82.2 g CO₂-eq/GJ, which is
16 lower than the ABE process.



1

2 Figure 7 Environmental impact (EI) breakdown per GJ of biofuel produced in two biorefinery systems
 3 using corn stover. ABE (Acetone-butanol-Ethanol) process and GMA (gasification and mixed
 4 alcohols) process.

5

6 Table 4 Environmental impact results for the ABE and GMA biorefinery processes for biofuel
 7 production

Result summary		
Technology	ABE	GMA
A. Embodied emissions in raw materials (t CO ₂ -eq/y)	107061	69484
B. Direct process emissions (t CO ₂ -eq/y)	611459	967393
Net power generation (kW)	37284	35724
C. Total energy contained in products (GJ/y)	2316590	3651814

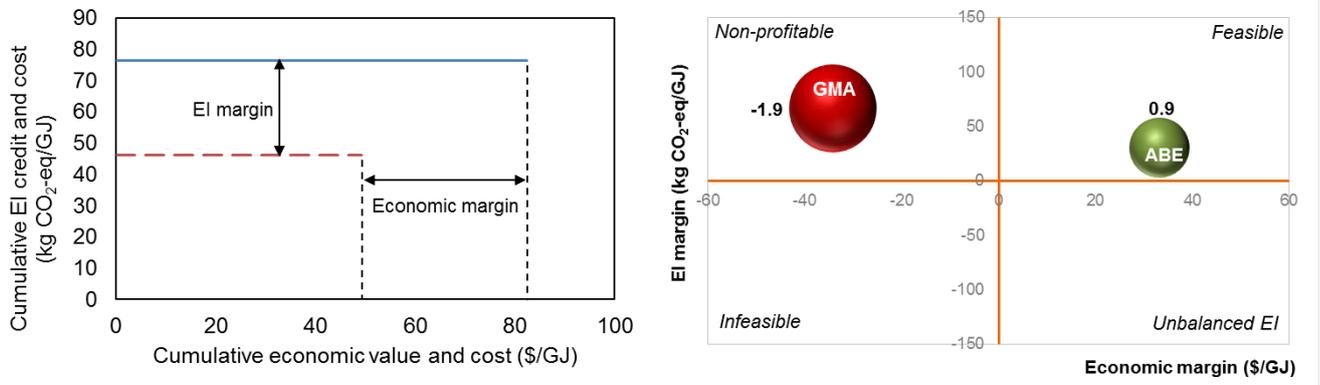
<u>Environmental impact credits from co-products</u>		
D. Acetone (t CO ₂ -eq/y)	60213	0
E. Electricity (t CO ₂ -eq/y)	163110	156287
Net emissions=A+B-D-E (t CO ₂ -eq/y)	495196	880590
F. Net emissions without direct process emissions=A-D-E (t CO ₂ -eq/y)	-116263	-86804
Gasoline displaced by biofuel products (t/y)	46611	82063
G. Environmental impact avoided (t CO ₂ -eq/y)	177121	311840
H. EI credit potential=G-F (t CO₂-eq/y)	293384	398644
I. EI credit potential without product credits=G-A (t CO₂-eq/y)	70061	242357

1

2 **3.8.EVEI analysis**

3 Figure 8 shows the plots used for EVEI analysis as explained in section 2.8. The EVEI analysis plot is
4 shown only for the ABE process as this was the only one profitable. Figure 8a shows that this process
5 generates about 34 \$/GJ of profit and an EI saving margin of 31 kg CO₂-eq/GJ with respect to gasoline.
6 Therefore, is located within the feasible region of the bubble chart in Figure 8b. The margins ratio
7 indicator for ABE process gives a value of 0.9 kg CO₂-eq of EI saving per \$ of profit. The corresponding
8 value for GMA process is -1.9 kg CO₂-eq/\$. As indicated by the bubble sizes, GMA provides more EI
9 margin but with negative economic margin, thus deemed to environmentally feasible but non-profitable.
10 From this analysis, it can be concluded that although GMA yields higher biofuel energy and
11 environmental impact margin it is not a cost-effective alternative to replace gasoline. Therefore, the

1 biochemical route or ABE biorefinery system needs to be adopted and analysed further to improve its
2 performance and develop a more detail process engineering.



3
4 Figure 8 a) EVEI analysis plot for ABE biorefinery system and b) EVEI margins analysis bubble chart
5 for feasibility analysis.

6 **4. Conclusions**

7 The Biorefinery Engineering Framework was developed in this paper by adopting a sequence of eight
8 steps involving: 1) biorefinery design problem definition, 2) data collection, 3) process synthesis and
9 simulation, 4) process integration, 5) resource recovery from residues, 6) utility system design, 7)
10 economic and environmental modelling and 8) EVEI analysis. The resource recovery step was important
11 to identify process opportunities from the biorefinery residual streams. This has proven to be the key in
12 making biorefineries energy self-sufficient and even be net producers of energy, which in turns offset
13 environmental emissions from displaced fossil-based sources and leads to net negative greenhouse gas
14 emissions. Another important contribution of the present work is the approach for simultaneous
15 evaluation of economic and environmental feasibility using EVEI margin analysis and its graphical
16 representations. The framework also offers transparent presentation of data collection and results for
17 informed decision making. The framework has been proved useful for two biorefinery systems
18 converting lignocellulosic corn stover into biofuels (ethanol, butanol and other alcohols). One system
19 uses biochemical route of ABE fermentation and the other uses thermochemical route of biomass

1 gasification with mixed alcohol synthesis (GMA). The results provide insights into the distribution of
2 costs and environmental impacts and why the GMA process is environmentally feasible but not
3 profitable, whilst ABE process is a feasible route that needs to be investigated for further improvement
4 and detailed process engineering.

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