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EXTENDED HIERARCHICAL DECOMPOSITION APPROACH FOR THE SYNTHESIS OF BIOREFINERY PROCESSES

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ABSTRACT

Synthesis of biorefinery processes have been of great interest in the research community and industrial practitioners for the past two decades. However, there is a lack of systematic approach for the synthesis of biorefinery processes, especially at the conceptual design level. This paper presents an extension on the systematic hierarchical decomposition approach (commonly known as the “Douglas’s hierarchical approach”) for the synthesis of biorefinery processes. Note that the Douglas’s hierarchical approach was originally developed for the synthesis of conventional chemical processes, and hence has various limitations when it is applied directly for the synthesis of biorefinery processes. These include unknown reaction stoichiometry, wide varieties of biomass feedstock, alternative conversion platforms, uncertain characteristic of biomass feedstock, etc. These challenges are now being addressed in the extensions proposed in this work for biorefinery process synthesis. Besides, additional tasks are included to assist reaction pathways screening at the early stage of design, while solid recovery system and material integration are being considered within the extended approach to maximise resource conservation and to minimise waste generation. The extended Douglas’s approach is demonstrated with a case study on the synthesis of palm-based biorefinery processes.

Keywords: conceptual process design, engineering economics, oil palm biomass

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INTRODUCTION

For the past century, the world has been heavily relying on fossil fuels such as coal, oil and natural gas as energy resources, as well as for petrochemical feedstock. Hence, numerous petroleum-based plants and refineries were being designed, constructed and established over the years. These accumulated experiences allow process synthesis methods for chemical processes and refineries to reach a sufficient state of maturity (Barnicki and Siirola, 2004). Some of the important developments up in the last century are available in some reviews (John, 2001; Li and Kraslawski, 2004). In addition, design heuristics were also being formed and applied in various areas in *process system engineering* (PSE), e.g. synthesis of heat exchanger networks (Kemp, 2007), separation trains (Morari and Faith, 1980), reactor systems (Rotstein et al., 1982, Lakshmanan and Biegler, 1996), and process flowsheet synthesis (Cremaschi, 2015).

Due to the various issues and challenges arise from the usage of fossil fuels and the increasing awareness on environmental sustainability, chemical industry begins to shift from the current fossil-based economy to a more sustainable economy based on renewable resources. Among the various types of renewables, biomass is recognised as one of the most promising resources to substitute fossil fuel as it contains most common elements (i.e. carbon, hydrogen, oxygen, and nitrogen) that are found in fossil resources but in different combinations. Biomass is mainly originated from crops, algae or crops residues, lignocellulosic material and municipal solid waste. These materials are usually incinerated, dumped in plantation as mulching material (common practise for countries with big agro-industry such as Malaysia), or disposed as waste material. Converting such materials into bioenergy and biomaterial in sustainable processing facilities could be beneficial in

fulfilling the future market and industrial demands. Thus, various policies and incentives from governmental funding agencies have been seen in recent years to promote the shift towards the sustainable generation of fuel and materials from biomass. Likewise, the utilisation and conversion of biomass have also undergone extensive researches in the past decade. The conversion pathway of biomass can now be generally categorised into biochemical, thermochemical, chemical and mechanical technologies. These processing pathways can be incorporated into a *biorefinery* (analogous to the conventional crude oil refineries), which may be defined as *a manufacturing facility that convert bio-based material into various products such as food, feed, fuels, chemicals, and energy*. A general concept for a biorefinery is shown in Figure 1 (IEA Bioenergy, 2013).

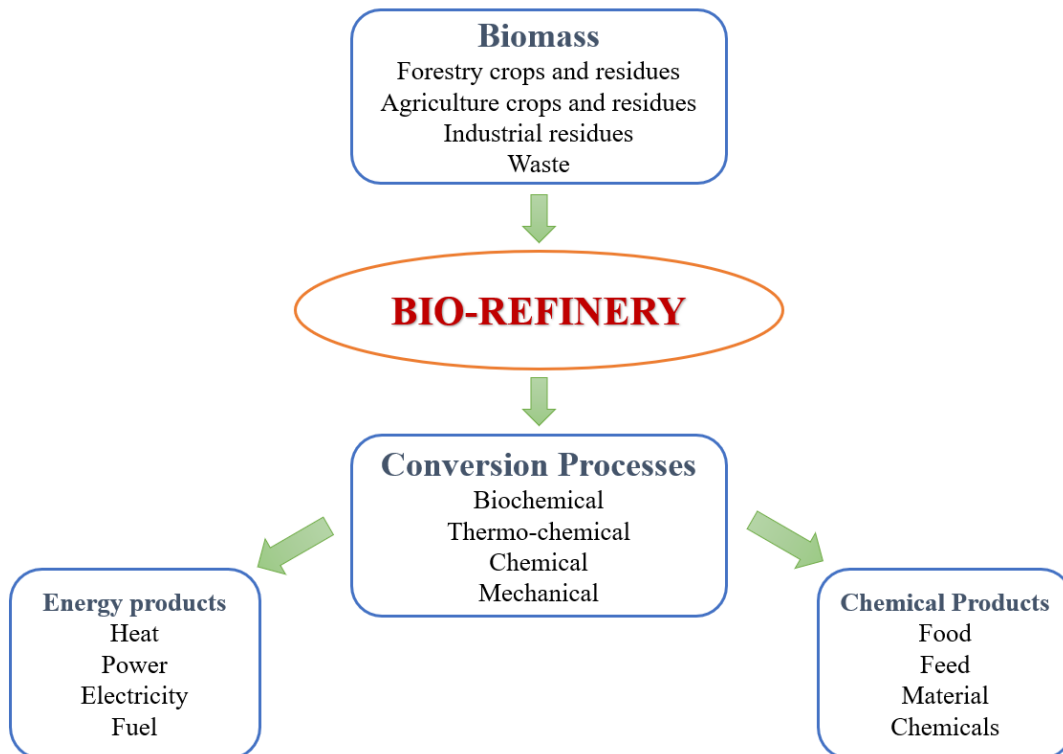


Figure 1. General concept of a biorefinery (IEA Bioenergy, 2013)

Despite the advantages and high interest placed upon the development of biorefinery, its large-scale application is still at research stage rather than real market implementations. This is mainly due to some important challenges such as the fluctuations of feedstock supply (due to seasonality), varying composition of biomass feedstock, complexity of technology and high processing costs for lignocellulose biomass (Upadhye et al., 2011, Mikkola et al., 2015). Note however that the cost is anticipated to reduce as technology matures (Balan, 2014). In order to attain higher economic revenue, biorefinery can undergo optimisation study in order to produce high value products (e.g. specialty chemicals), or a large volume of low value products (e.g. fuel). In addition, biorefinery could also provide a platform for holistic exploration of available resources to address the issues of future energy and material requirements (Foston and Ragauskas, 2012).

Conceptual process design and synthesis for biorefinery

In order to overcome the challenges and to accelerate the development of a biorefinery, conceptual process design could play an important role. In particular, conceptual process design can be used to generate alternative process flowsheets to convert biomass to products based on experimental analysis and information. To date, alternative approaches have been developed for the synthesis of biorefinery processes, such as the hierarchical approach (Ng et al., 2009, Conde-Mejía et al., 2015), mathematical optimisation approach (Bao et al., 2011, Ponce-Ortega et al., 2012, Pham and El-Halwagi, 2012, Ng and Ng, 2013, Yuan and Eden, 2016, Rizwan et al., 2019, Tey et al., 2020), insight-based approach such as carbon-hydrogen-oxygen ternary diagram (Tay et al., 2011), automated targeting technique (Ng, 2010; Tay and Ng 2012) and graph theoretic approach (Yeo et al., 2020). For the hierarchical approaches (Ng et al., 2009, Conde-Mejía et al.,

2015), decomposition strategy is normally applied. A series of hierarchical decisions were proposed at different stages of the process synthesis to guide the designers in making decision. Meanwhile, for the mathematical optimisation approaches, a generic superstructure is first developed to represent all possible alternatives, and the developed models is then solved via mathematical optimisation platforms. Different configuration of integrated biorefinery have been developed, e.g., palm-based biorefinery (Ng and Ng, 2013), fast pyrolysis-gasification for production of liquid fuels and propylene (Yuan and Eden, 2016), microalgal biorefinery (Rizwan et al., 2019), seaweed-based biorefinery (Dickson and Liu, 2019), etc. Besides, research efforts have also been reported for techno-economic analysis for biomass to energy pathway (Sassner et al., 2008, Pokoo-Aikins et al., 2009, Wan et al., 2016a, Bressanin et al., 2020), biomass to value-added products (Sadhukhan et al., 2008; Wan et al. , 2016b), optimal design in integrated biorefinery with molecular design (Chemangattuvalappil and Ng, 2013; Ng et al. 2015a, 2015b; Dickson et al., 2020), as well as the incorporation of environmental perspective (Sammons et al., 2008, Machado et al., 2018; Dickson and Liu, 2019) and safety metrics (Pokoo-Aikins et al., 2010). As mentioned previously, most works on mathematical optimisation were developed based on superstructure-based methodology; the latter is solved to determine the optimal products/processes for a biorefinery. The main limitation for the abovementioned approach is that, it requires considerable amount of computational effort to solve for the optimum design solution. Moreover, this method faces great difficulty in optimising design problems which are often under-defined with high level of uncertainties, as commonly encountered in biorefinery processes (Li and Kraslawski, 2004).

As compared to mathematical programming, limited work have been carried out using hierarchical decomposition approach for the systematic synthesis of biorefinery processes. The latter decomposes the complex tasks of process design into a hierarchical series of sub-problems, such as reactor, input-output-recycle structure, separation and energy recovery subsystems. The process design is then being completed sequentially for the most promising alternatives, which could latter serves as a base case, where other alternatives may be developed and subjected to further optimisation exercises. Thus, this approach has an advantage of allowing quick evaluation of new process alternatives. It also provides a systematic framework to rapidly evaluate the technologies involved. Moreover, it could also serve as a guide for further research effort to speed up the maturity of biorefinery technologies (Upadhye et al., 2011). However, most of the developed work based on hierarchical decomposition approach were mainly focused on thermochemical conversion pathway (which is meant for biofuels production) rather than bio-chemical or biological conversion pathways (Upadhye et al., 2011, Hossain et al., 2010). The latter encounters different challenges during the synthesis tasks. Therefore, it is important to extend the hierarchical decomposition approach for different conversion pathways and technologies to effectively broaden the scope and understanding of biorefinery processes.

Hierarchical decomposition approaches for chemical process design

Several important hierarchical decomposition approaches have been proposed to synthesise chemical processes. Figure 2 shows these models, which include the Siirola and Rudd's model (Siirola and Rudd, 1971; Seider et al., 2019), the Douglas model (Douglas, 1985, 1988) and the Onion model (Linnhoff et al., 1982; Smith, 2016).

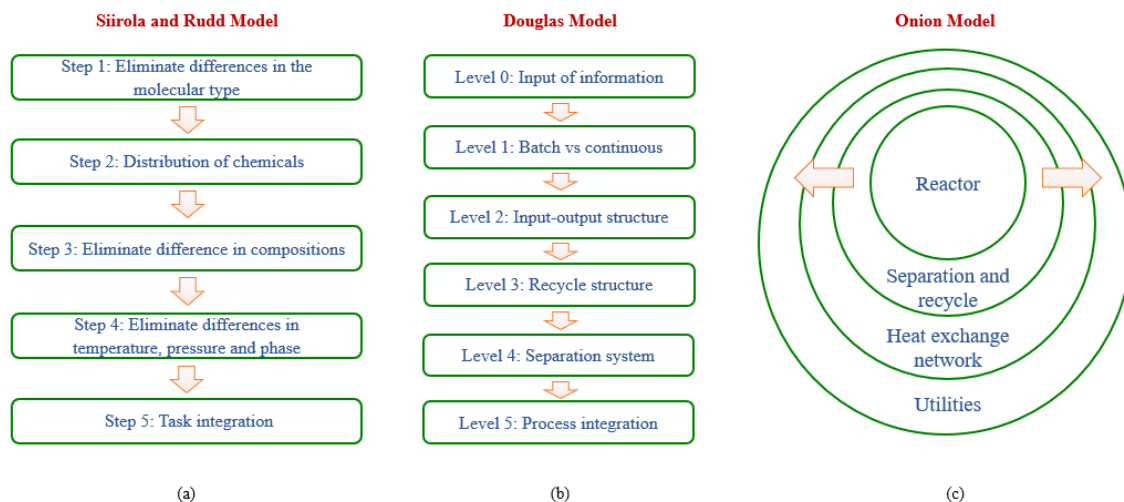


Figure 2. Important hierarchical decomposition approaches (a) Siirola and Rudd's model, Douglas model, and (c) the Onion model

Among these approaches, the Douglas' model is arguably the most widely adopted hierarchy. It has been refined and incorporated into other process design methodologies (Emets et al., 2006, Korevaar, 2004). It has been included in modern chemical engineering textbook (Seider et al., 2019), as well as for the training of industrial personnel (Harmsen, 2004). The seminal work for the Douglas' model first proposed in year 1985 (Douglas, 1985), with the aim to generate a reasonably good flowsheet for a design base case. In the follow-up work, solid system was added to the existing vapour and liquid separation systems (Rossiter and Douglas, 1986a, 1986b). The detailed illustration of the procedure is found in a textbook (Douglas, 1988). The model was later extended to include waste minimisation effort (Douglas, 1992) and process synthesis involving renewable energies (Upadhye et al., 2011). Note however that the existing procedure does not fit for the use of biorefinery process design directly, due to the existence of technology differences, and

uncertainties of biorefinery processes as compared to the conventional chemical processes. Hence, the main subject of this work is to propose modification for the Douglas's hierarchical decomposition approach so to suit its use for current and future biorefinery process synthesis. The extended hierarchical approach will be demonstrated with an example, in which oil palm solid biomass is used as feedstock. Oil palm biomass is selected as the raw material of the biorefinery process due to large quantity of oil palm waste available in Southeast Asian countries such as Malaysia and Indonesia (the world's major exporters of palm oil).

METHODOLOGY – EXTENDED DOUGLAS' MODEL FOR BIOREFINERY PROCESSES

The overall structure of the extended hierarchical decomposition approach remains the same as the original work (Douglas, 1988). Note however that direct application of the original Douglas's hierarchical model for biorefinery process synthesis may not be effective due to the differences between biorefinery and conventional chemical processes. Hence, various extensions are proposed in this work, so to suit for the synthesis of biorefinery processes. In the following, the limitations of the original Douglas' model is discussed. The overall framework is shown in *Table 1*. The newly added elements at each level of the model are next discussed, so to reflect the limitations and challenges faced in biorefinery process synthesis with the original Douglas' model.

Table 1: Extended hierarchical decomposition approach for biorefinery process synthesis

Level	Required decision task(s) or information
0	Input Information
	<ol style="list-style-type: none"> 1. Consideration of forward/backward synthesis* 2. Reaction pathways evaluation, screening, and selection* 3. Information of reactions (e.g. stoichiometric coefficients for biochemicals*) and catalysts 4. Characterisation of biomass* 5. Demographics, availability of raw materials* 6. Products specification* 7. Any processing constraints 8. Other plant and site data 9. Physical properties and chemical properties of all components 10. Information concerning safety, toxicity, and environment impact of the materials involved in the process (to consider basic environment impact analysis, e.g. CO₂ reduction, value of carbon credits, etc.*) 11. Estimation of thermodynamic efficiency and lost-work with second law analysis for energy-intensive processes* 12. Cost data for raw material, product and by-products, equipment, and utilities
1	Batch versus Continuous
	<ol style="list-style-type: none"> 1. Production rate 2. Market forces 3. Scale-up problems 4. Operation mode
2	Input-Output Structure
	<ol style="list-style-type: none"> 1. How many reaction systems are required?* 2. Should we standardise (e.g. mechanical treatment such as milling, crushing, etc.) and purify the feed streams before they enter the reaction systems?* 3. Should we remove or recycle a reversible by-product? 4. Should we use a gas recycle and purge stream? 5. Should we not bother to recover and recycle some reactants? 6. How many product streams will there be? 7. Mass balance for defined reaction systems.* 8. What are the design variables for the input-output structure, and what economic trade-offs are associated with these variables?
3	Recycle Structure of the Flowsheet
	<ol style="list-style-type: none"> 1. Is there any separation between the reactors system?* 2. How many recycle streams are required? 3. Do we want to use an excess of one reactant at the reactor inlet? 4. Is a gas compressor required? What are the cost? 5. What are the operation requirements for reaction systems?* 6. Do we want to shift the equilibrium conversion? How? 7. How do the reaction systems and recycle system cost affect the economic potential?
4	Separation System
	<ol style="list-style-type: none"> 1. General structure <ul style="list-style-type: none"> • Do we need any phase split between solid, liquid and vapour materials? 2. Vapour recovery system <ul style="list-style-type: none"> • Do we need a vapour recovery system? • What is the best location? • What type of vapour recovery system is the cheapest? 3. Liquid recovery system <ul style="list-style-type: none"> • Do we need a liquid recovery system? • What is the best location? • Methods to remove contaminating light ends, and destination of the light ends? • What separation can be made by distillation, how we handle azeotropes in the recycle stream?

	<ul style="list-style-type: none"> • Column sequencing of distillation system? • If distillation is infeasible, what methods should we use for separation? <p>4. Solid recovery system**</p> <ul style="list-style-type: none"> • Do we need a solid recovery system? • What is the best location? • What solid recovery system should be used?
5	Task Integration
	<p>1. Any ancillary equipment required?***</p> <ul style="list-style-type: none"> • Solid transport, pump, compressor, heater, cooler, intermediate storage and buffer tank, mixing tank <p>2. Material recovery and integration*</p> <ul style="list-style-type: none"> • What resources do we have for recovery (e.g. purge stream, biomass residues)? • Waste and material minimisation and integration for vapour, liquid and solid <p>3. Heat integration</p> <ul style="list-style-type: none"> • How to generate heat and electricity from biomass waste (CHP)? • Minimum heating and cooling requirement • Minimum no. of exchangers and area required

*Proposed extension to the Douglas's hierarchical decomposition approach (Douglas, 1988)

** Adapted from Rossiter and Douglas (1986) and Upadhye et al. (2011)

***Adapted from Siirola and Rudd (1971)

Level 0 – Input Information

Firstly, the original Douglas's hierarchical approach dives straight into defining the reactions and reacting conditions for the chemical process, without the screening of alternative processes. For conventional chemical processes, economic potential calculation are commonly used to screen large number of alternative processes; the latter may be obtained from laboratory experiments or commercial processes. However, for biorefinery processes, not all reaction stoichiometry are made available. Besides, there exist a wide variety of biomass feedstock (e.g. palm biomass, rice husk, coconut shells) and alternative conversion platforms that can be evaluated to produce various products. Therefore, several tasks are required to aid the screening of alternative processes, which are to be added at Level 0.

A common approach for chemical process design is backward synthesis, as shown in Figure 3(a). This approach is used when the product is known and the process for its

production is to be designed, while its feedstock is to be sorted. However, forward synthesis approach is often encountered for biorefinery process design (see Figure 3(b)). This is due to the situation where biomass or waste stream are already available for use as feedstock, hence the design task is to determine what value-added products are to be produced, apart from synthesising the process flowsheet. Therefore, it is important to consider both backward and forward process synthesis approaches for biorefinery process synthesis.

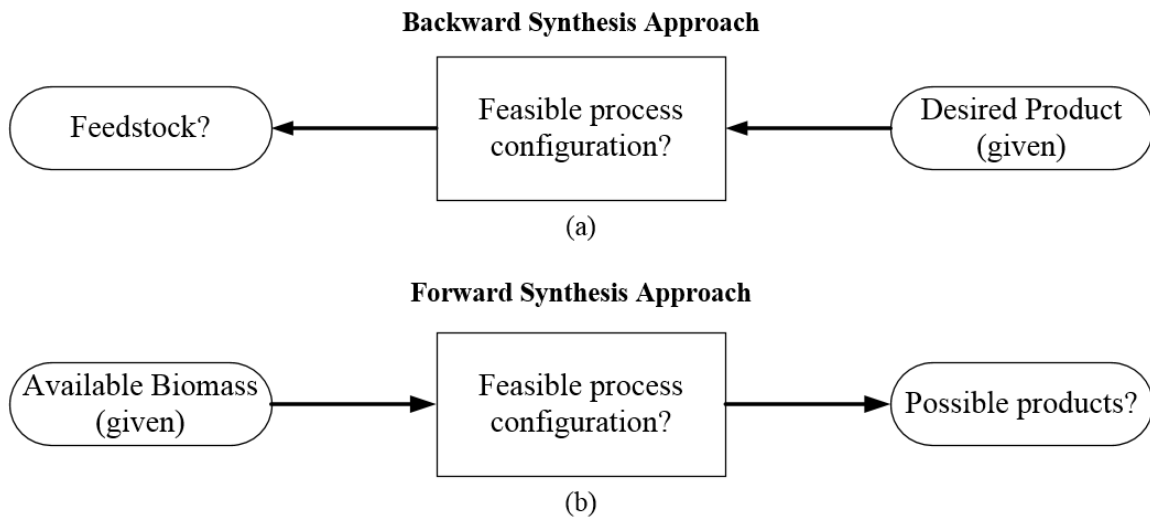


Figure 3. (a) Backward synthesis approach; (b) forward synthesis approach (adopted from Pham and El-Halwagi, 2012)

Due to the lack of reaction screening task in the original Douglas's approach, this task is now added at Level 0 to aid in the pre-screening activity, as shown in Figure 4. The design engineer is required to consider either adopting forward or backward synthesis approach. For the latter, the associated conversion pathways to produce specific products are first collected. On the other hand, characterisation of biomass is first conducted for forward synthesis approach in order to understand the properties of the biomass, prior to the collection of suitable conversion pathways. This allows the effectively utilisation of biomass feedstock. For cases where raw materials or products were not pre-determined,

other design constraints such as plant location, availability of raw material and product market demand should be considered in the selection of raw material and/or products of the process.

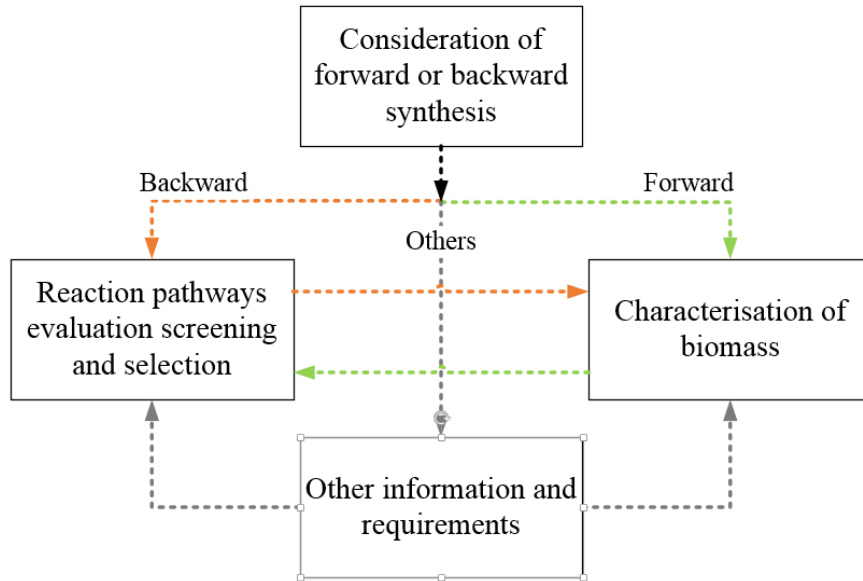


Figure 4. Reaction screening task at Level 0

For reaction pathways screening, a general guideline comprising of the various common conversion routes (physical, thermochemical, biological and chemical) for biomass is compiled and shown in Figure 5. Note that this guideline is not extensive and can be expanded to incorporate other conversion technologies or new innovations in the future.

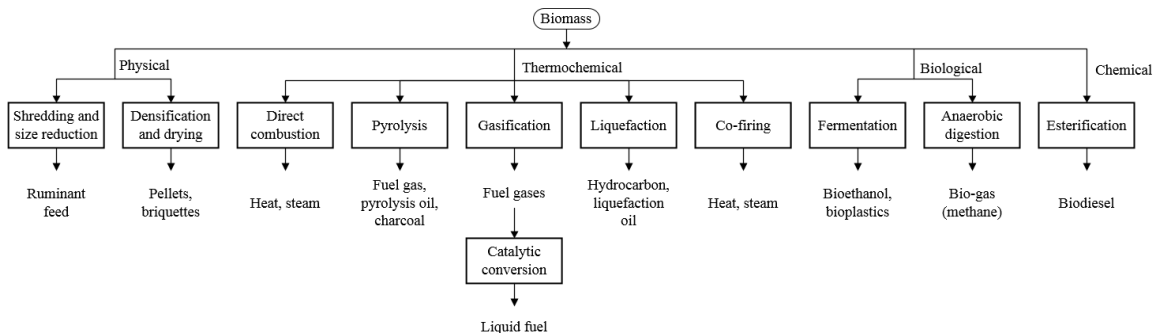


Figure 5 reaction pathways screening at Level 0 (adopted from Cherubini et al., 2009)

According to the original Douglas's approach, the screening and evaluation of potential reaction alternatives for conventional chemical processes are mainly based on economic profitability, environmental impact and inherent safety. However, for the case of biorefinery, it is important to consider the different degree of complexity and maturity for each individual biorefinery technology. In addition, there are possibilities that a combination of several synthesis routes to produce multiple products within an integrated biorefinery to be technically or economically infeasible (Conde-Mejía et al., 2015). Thus, it is challenging to judge the technological and economical risks for a given biorefinery process, especially when information about these technologies are not fully known. With regards to this, an approach developed by the IEA Bioenergy Task 42 known as the "Biorefinery Complexity Index (BCI)" may be used for the evaluation of process complexity (Jungmeier et al., 2014). The BCI considers the number of features added into a biorefinery facility, and the state of the technologies based on their readiness level, i.e. "basic research" to "system proven and ready for full commercial deployment". In other words, the criteria for biorefinery processes evaluation is extended beyond economic potential alone, where other aspects such as complexity and maturity of the processes,

energy demand, thermodynamic feasibility, etc. are considered. This approach has been demonstrated by Ng et al. (2009) and Tan et al. (2019).

In order to solve mass and energy balances for a biorefinery process, information involving reaction (e.g. stoichiometric coefficients) and thermophysical properties (e.g. densities, heat capacities, enthalpies and entropies of formation) are crucial, and shall be established in early stages prior to process design. An example of establishing the key components and their parameters has been demonstrated in the work of Dunlop et al. (2013).

Another challenge of biorefinery process lies with its biomass feedstock, which is specific, complex and not highly predictable. Therefore, characterisation of biomass (e.g. bulk, physical and chemical properties) need to be determined at the initial stage. Doing this allows better understanding of the biomass properties in their raw complex form. With biomass characterisation, suitability of a given biomass to be used as feedstock for subsequent conversion technologies is identified. It provides essential information to support the subsequent design of feed purification system at Level 2. Furthermore, it also allows opportunity for the blending of different biomass types (but with similar properties) as feedstock, in order to increase the production capacity and reduce impact of feed supply fluctuations. The basic parameters that are suitable for biomass characterisation are found in Appendix A.

Note that biomass supply is subjected to fluctuations due to weather conditions, seasonality and the availability for a given geographical region. Hence, the production rate of a biorefinery is highly dependent on the availability of biomass feedstock. Other than that, biorefinery products are commonly found in solid form. Thus, apart from product

purity, product specifications such as desired particle size and distributions, as well as bulk properties should be pre-defined for these solid products.

The conversion of biomass as value-added products in biorefinery also entail CO₂ emission reduction. Hence, it will be valuable to perform some preliminary assessment on the extent of CO₂ reduction, and the amount of carbon credit gain, while information concerning safety, toxicity, and environment impact are collected. Besides, it is also good to perform estimation on thermodynamic efficiency and lost-work with second law analysis for energy-intensive biorefinery processes, e.g. biofuel production (Dunlop et al., 2013).

Level 1 – Batch versus Continuous

At this level, the operation mode of biorefinery processes are to be decided, based on factors such as production rate, market demand and scale-up problems. Biorefineries with thermochemical conversion platform and biofuel projects are commonly designed to be operated in large scale and continuous operation mode. Doing so allows the production of high volume of lower value-added fuel products with lower cost. The main benefits of operating a continuous mode process include consistent and higher quality fuel. However, some biomass conversion pathways that produce low volume of high value-added speciality chemicals are to be operated in batch mode. Hence, there are possibility that a hybrid continuous and batch processes to co-exist in an integrated biorefinery. This can be achieved by having intermediate storage tanks between batch units, or with parallel batch cyclical units (Upadhye et al., 2011). Note that no modification was made for this level, i.e. the hierarchical decision in the original Douglas' model holds valid.

Level 2 – Input-Output Structure of Flowsheet

At this level, the input and output structure of the flowsheet is to be established. The number of reaction systems is being determined before the feed components is allocated to the reaction systems. The mass balance of the process can then be carried out by matching the input and output components for the reaction systems, and next for the whole process.

In the original Douglas's approach, it is easy to calculate the overall material balance at Level 2 for conventional chemical processes, where product(s) is made based on given production rate, reaction stoichiometry, and product distribution correlations. However, for biorefinery synthesis, several processing technologies may be integrated, in which multiple products are made. Therefore, material balance calculation is challenging for biorefinery processes as some of the pathways and technologies are complex, and suffer with insufficient stoichiometry information. Therefore, it is proposed that the “defining the number of reactor systems” task to be shifted from Level 3 (original Douglas's approach) to Level 2. Doing this would ease the material balance calculation for the individual reactor systems with available information (e.g. yield and selectivity), before the subsequent calculation is made for the overall process. Reaction systems of biorefinery processes may include thermochemical (e.g. gasification, combustion, pyrolysis), biological (e.g. enzyme hydrolysis, fermentation) pathways, and other conventional chemical conversion processes.

Besides, the decision for feed purification at Level 2 in the original Douglas's model is also being expanded to consider a series of feed purification and standardisation

tasks for biomass, prior to entering the reaction systems. Feed purification or standardisation of biomass is essential to ensure consistent biomass feed being supplied to the process, in order to fulfil the pre-requisite requirement of the reaction systems. Note that feed purification involves processes that do not change the chemical composition of the biomass. These include pH adjustment, mechanical processes (particle reduction, grinding, etc.), washing operation (for impurities removal), drying and concentration (moisture content adjustment). Moreover, sterilisation which is required in biological conversion, pharmaceutical and food processes can also be considered as purification operation. Since feed purification operations are usually energy- and cost-intensive (Conde-Mejía et al., 2015), it is included in the economic potential (EP) evaluation at this level, as proposed by Upadhye et al. (2011), given as in Equation 5 that follows.

$$EP_2 \left(\frac{\$}{\text{yr}} \right) = \text{Product and byproduct value} - \text{Raw material and processing cost} - \text{Waste disposal cost}$$

(5)

Level 3 – Recycle Structure of the Flowsheet

After the input-output structure of the system is established at Level 2, details and configuration for each reaction systems are considered at this level. Any requirements for separation system between and after the reaction systems are treated as black boxes at this stage (to be evaluated with more details at Level 4). However, separation system can be considered at this level for special cases with process intensification, such as reactive distillation, membrane reactors, that has good potential to enhance the efficiency of the conversion technology.

An important new addition to Level 3 is the operational requirements that are specific for biological conversion platforms. These include dissolved oxygen content, agitation, pH, nutrient deficits, anaerobic or aerobic conditions. Besides, possible recycling opportunities to improve the conversion for reversible reactions should be considered at this level. For recycling system, the original hierarchical approach (Douglas, 1985) distinguishes between gaseous and liquid recycle systems, as gaseous recycle streams requires expensive compressors. It is common for petrochemical processes to handle large number of gaseous streams. However, for biorefinery processes, solid and liquid streams are more dominant (Yuan et al., 2013). Note that some thermochemical conversion platforms in biorefinery would still involve gaseous streams recycling, e.g. syngas recycling for the synthesis of bio-fuel (Consonni et al., 2009). Therefore, the annualised capital cost of the reaction systems and transfer cost (which include pump and compressor, if applicable), are both included in EP evaluation of this level, following the original model (Douglas, 1985). This is given in Equation (6) that follows.

$$EP_3 \left(\frac{\$}{yr} \right) = EP_2 - \text{Annualised reactor(s) cost} - \text{Annualised transfer cost} \quad (6)$$

Level 4 – Separation System

This level considers the synthesis of separation system to recover vapour, liquid and solid components which were considered as black boxes at the previous level. The original Douglas's model is heavily dedicated for vapour and liquid materials. Note that the extension to solid processing steps such as crystallisation, filtration and drying has been developed by Rossiter and Douglas (1986). However, this early work was mainly focused

on moderate to high volume and continuous processes, as well as inorganic solid products that are made from liquid or solid feeds. For the case of biorefinery processes, the design for solid and slurry separations are critical, as various types of solid biomass are involved. It is necessary to consider a wider range of solid separation steps in both thermochemical and biochemical conversion platforms, as biorefinery processes utilise lignocellulose waste that is commonly found in solid state.

In the original hierarchical approach, the phase of the process streams needs to be determined before the phase split operations is considered. Phase split is considered prior to any individual phase recovery system, as it is the cheapest separation method (Douglas, 1985). Figure 6 presents some examples of separation technologies for different phases. Phase split between vapour and solids are required especially in biofuel gasification which involve separation of tar or ash from syngas. For solid-liquid splits, it can be categorised as homogeneous or heterogeneous mixtures. Separation technologies that are suitable for homogeneous solutions include drying, extraction, crystallisation, precipitation and membrane, while separation of heterogeneous solid-liquid mixture can be conducted through decantation, hydrocyclones, filtration, centrifugation, settling, sedimentation, floatation, leaching, and solid drying.

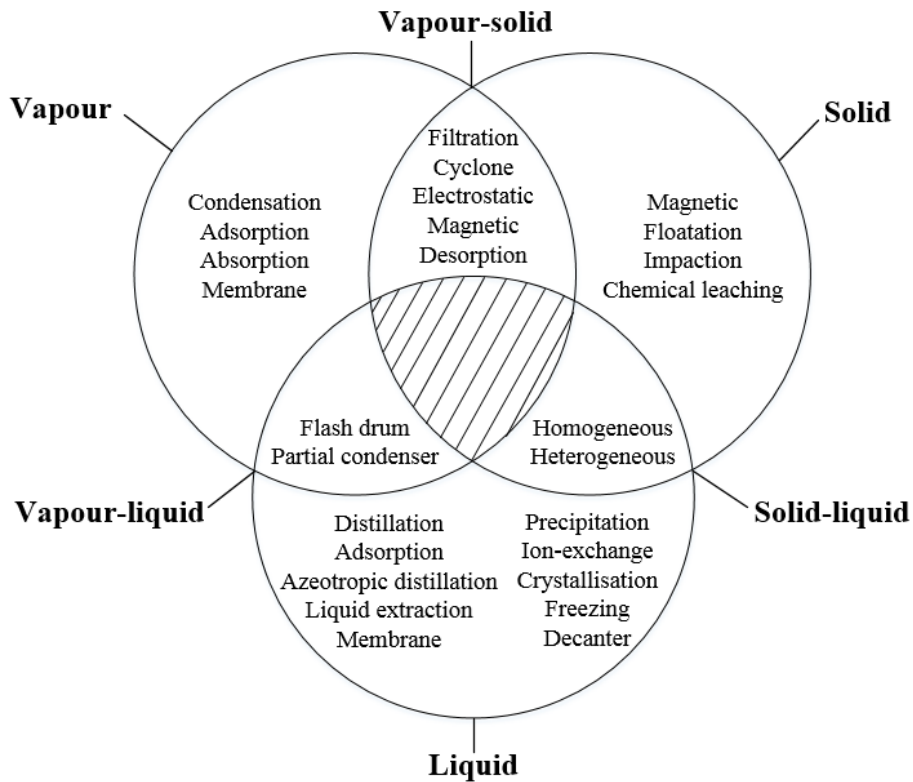


Figure 6. Examples for technologies involved in separation systems (Yang et al., 2013, Wilcox, 2009)

When the process stream exist as a single phase, only specific individual phase separation system is considered. For vapour and liquid recovery systems, extensive discussions were reported by Douglas (1985). Vapour recovery system can be considered for purge stream, gas-recycle stream, or flash vapour stream, with heuristics to prevent significant loss of valuable material in the purge stream, or toxic components present in the recycled stream, etc. For the design of liquid recovery system, some of the light end components might be entrained after vapour recovery and present within the liquid streams. Thus, consideration for light-ends removal is necessary, especially if it will lead to contamination for the product or reactor (if it is recycled). For solid recovery system, physical or chemical separation methods can be considered. The selection and configuration sequence of the separation technologies needs to take into consideration of

the feasibility, energy consumption, as well as cost of equipment and operation. The economic potential in this level which is adapted from Douglas (1985) accounts for the cost of separation system.

$$EP_4 \left(\frac{\$}{\text{yr}} \right) = EP_3 - \text{Annualised separation system cost} \quad (7)$$

Level 5 – Task Integration

After the process consisting of reaction and separation systems are synthesised, the flowsheet of the biorefinery is almost complete. At this level, the addition of ancillary equipment such as solid and liquid transport systems (e.g. pump, compressor), utility exchanger (e.g. heater, cooler), auxiliary tanks (e.g. buffer, mixing) are added if necessary. Other than that, task integration should consider both heat and material recovery at this level, given that detailed mass and energy balances have been carried out for the selected processes, in order to improve cost savings of the process. Material recovery has been extensively researched since mid-1990s (i.e. after Douglas' approach was established) and has reached mature stage in the past decade. Various insight-based (e.g. pinch analysis) and mathematical-based techniques (Foo, 2013; El-Halwagi, 2017) have been proposed for materials recycling (e.g. water, solvent, etc.) so to minimise waste generation. Doing this leads to cleaner process design (Foo and Ng, 2013). Note that various types of biomass residues can be used for the generation of heat and electricity for the biorefinery facility. Hence, the economic potential of this level is extended to include energy and resources savings from heat and material integration, as well as revenue from waste utilisation.

$$EP_5 \left(\frac{\$}{\text{yr}} \right) = EP_4 - \text{Cost of ancillary equipment} \\ + \text{Savings through heat and material integration} + \text{Revenue from waste utilisation} \quad (8)$$

CASE STUDY

The extended hierarchical approach is demonstrated with a case study, with palm biomass as feedstocks. Oil palm frond (OPF) is the most abundant by-product in the oil palm plantation. It is available throughout the year due to harvesting or pruning activities. In most cases, OPF is left rotten in the plantation for soil erosion control and long term benefit of nutrient recycling. In this case study, the OPF frond is to be harvested on site so to obtain its basal (lower portion of the frond) which is rich in sugar and cellulose content. The OPF basal can be used for the production of biofuels and bio-based chemicals, while the remaining part of the OPF that are rich in nutrients can be left in the plantation as soil fertilisers (Omar, 2014). In this case, the use of extended Douglas model is illustrated for the evaluation of different alternatives, in order to minimise cost, environmental impact and safety hazards.

Level 0: Input Information

For this case study, forward synthesis approach is being considered as OPF has been determined as the feedstock. Characterisation of the biomass is hence conducted to obtain information such as the ultimate and proximate analysis, sugar content, chemical components and physical properties of OPF (see Appendix B). From the collected information, it is found that OPF can be pressed to obtain its sugar-rich juice. On the other

hand, the OPF fiber which is low in lignin and high in holocellulose can be hydrolysed by enzyme to produce sugars such as glucose and xylose (Zahari et al., 2014). In summary, OPF has good potential to be used as a fermentable feedstock, to become value-added products via biological conversion pathways.

Figure 7 presents some of the feasible conversion technologies for OPF into value-added products. Literature searches reveal that OPF juice which is rich in sugar is mainly used as fermentation feedstock for biological products, while its fibres can be used to produce briquettes, bio-composites or ruminant feed by physical processing (Abdullah et al., 2015, Che Maail et al., 2014, Tan et al., 2016, Zahari et al., 2014). The economic evaluation for the conversion pathways (see details in Appendix C) shows that the production of Poly(3-hydroxybutyrate), i.e. P(3HB) bioplastics from glucose has the highest gross profit of 1,800 USD/t of P(3HB) plastic. The selected pathway is via fermentation process, using *Cupriavidus necator* as bacteria cells. The glucose is to be sourced from both OPF juice and saccharification of the OPF fibre.

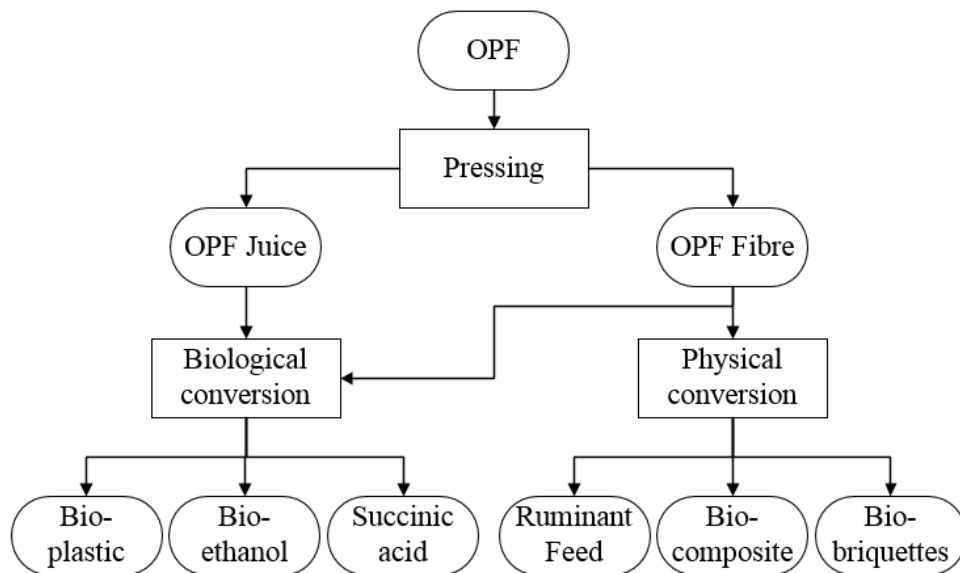


Figure 7. Conversion technologies for OPF into value-added products

Further evaluation of the reaction pathway from OPF to P(3HB) bioplastics defines that saccharification of the OPF lignocellulose fibre would produce both glucose and xylose sugars. Fermentation of glucose into P(3HB) has high productivity (Zahari et al., 2014), but the yield of P(3HB) is low for xylose. With regards to xylose and glucose co-culture fermentation process, xylose uptake remains as a challenge in industrial application and it is often treated as waste if it is co-fermented with glucose. Twofold amount of xylose has to be consumed for P(3HB) formation and this results in higher amount of oxygen supply, CO₂ release, and cell debris discharge (Moysés et al., 2016). Thus, xylose can be separated from glucose prior to P(3HB) fermentation process for other conversion pathways. It can be oxidised into xylonic acid, undergoes hydrogenolysis to form xylitol or fermented into bioethanol. The latter pathway is selected as bioethanol can be used as a biodegradable solvent for the downstream purification process for P(3HB) bioplastics.

With these additional pre-screening steps at Level 0, multiple solutions can be generated but only a small number of solutions is screened for further evaluation. This is advantageous as detailed assessment for all process alternatives is not practical as it required substantial amount of information, as well as considerable time and resources for the analysis (Cheali et al., 2015). Furthermore, integration of various processes within the biorefinery process design can be conducted at this early stage of design to ensure effective utilisation of the biomass feedstock. Other than economic potential, criteria such as waste-to-product conversion may also reduce environmental problems, high energy and economic cost for waste treatment, as well as allowing feasible process design to upgrade by-products or wastes into useful products. Therefore, this extended hierarchical model

which involves reaction pathway screening and evaluation tasks could further enhance the functionality of biorefinery process.

After selection of the appropriate reaction pathways through screening, other input information required are gathered (see Appendix D). Some of the main input information are summarised in Table 2.

Table 2: Input information about reactions, demographics and availability of raw materials at Level 0

<p>P(3HB) fermentation $C_6H_{12}O_6$ (Glucose) + 2.049O₂ + 0.264NH₃ → 1.059CH₂O_{0.5}N_{0.25} (Cell) + 2.5116CH_{1.5}O_{0.5} (P3HB) + 2.4294CO₂ + 3.4536O₂ (1)</p>	
<p><u>Yield:</u> 40% g/g of sugar consumed <u>Requirements:</u> 31°C, pH 6.80, DOT 20% of saturation, reactor concentration maintained at 50% (v/v), 48hrs <u>Bacteria cell type:</u> <i>C. necator</i> NCIMB 11599</p>	Yang et al. (2013)
<p>Bioethanol fermentation $3C_5H_{10}O_5$ (Xylose) → 5C₂H₅OH (Ethanol) + 5CO₂ (2)</p>	
<p><u>Yield:</u> 0.32 g ethanol/g xylose <u>Requirement:</u> 26°C, pH 4.5, DOT at 95% saturation, 84hrs <u>Bacteria cell type:</u> <i>Pichia stipites</i> NRRL Y-7124</p>	McMillan (1993), Slininger et al. (1990)
<p>Saccharification of OPF fibre $(C_6H_{10}O_5)_n$ (Cellulose) + nH₂O → nC₆H₁₂O₆ (Glucose) (3) $(C_5H_8O_4)_n$ (Hemicellulose) + nH₂O → nC₅H₁₀O₅ (Xylose) (4)</p>	
<p><u>Conversion:</u> 70% of holocellulose in OPF fibre (80%) converted to sugars <u>Requirement:</u> 50°C, 48 hrs, <u>Biocatalyst:</u> Cellulase</p>	Wyman et al. (2004)
<p>Demographics, availability of raw materials and plant production capacity</p>	
<p><u>Demographics:</u> Malaysia <u>Raw material availability:</u> Available throughout the year 300,000 t/y OPF, can be blended with oil palm trunk</p>	Zahari et al. (2015)

Level 1: Batch versus Continuous

For this case study, batch operation mode is selected as the harvesting of OPF is carried out during day time. Note that the storage of OPF as feed supply for a continuous operation mode is not desired due to the rapid sugar degradation over time in the OPF petiole (Che Maail et al., 2014). Besides, a large amount of OPF fibre slurries is to be handled for the enzyme saccharification reaction, which requires slow transportation rate. Furthermore, the major biological conversion platforms have long reaction and retention time (typically 48-84 hours), which dictate the use of batch operation mode.

Level 2: Input-Output Structure of Flowsheet

Figure 8 (a) shows the detailed input-output diagram for the process. Note however that biocatalyst (cellulase, *Pichia stipites* NRRL Y-7124 and *C. necator* NCIMB 11599), solvent for downstream separation, culture medium and seed fermenter are excluded. Figure 8(b) on the other hand, shows the detailed feed purification tasks involved.

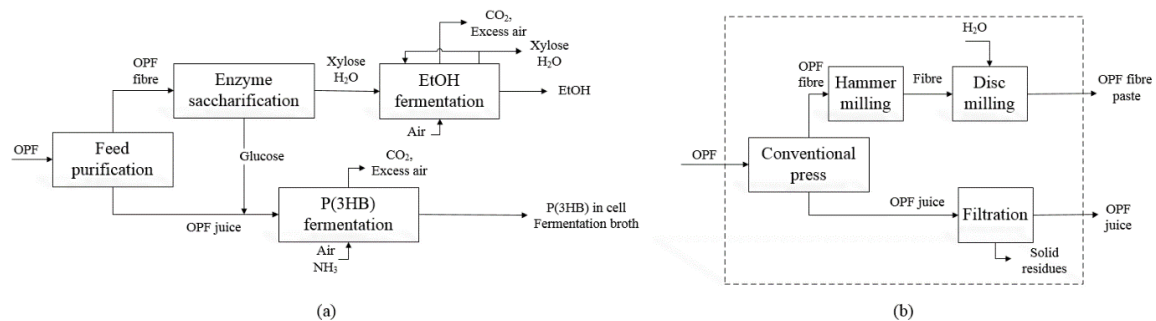


Figure 8. (a) Detailed input-output diagram for the process; (b) detailed feed purification tasks

As shown in Figure 8, OPF is being purified into its fibre and glucose-rich juice components, before they are fed to the reaction systems. Three reactions are involved in

the process, i.e. enzyme saccharification that converts OPF holocellulose fibre into xylose and glucose, bioethanol (EtOH) fermentation which converts xylose into ethanol, and P(3HB) fermentation which uses bacteria to produce P(3HB) bioplastics from glucose as storage compounds under growth limiting conditions (see details in Table 2). For the purification tasks, OPF that is moisture-rich is to be pressed to recover its juice from the biomass. The length of OPF fibre is also reduced by milling operations to improve the yield of enzyme saccharification (Zahari et al., 2014). Besides, filtration unit is required to purify the juice from any solid residues. Table 3 shows the product streams at this stage and their respective destinations.

Table 3: Source and destination of product streams

Products	Source	Destination
OPF fibre residue and lignin	Filtration after enzyme saccharification	Used as solid fuel for steam and power generation
Solid residues from OPF juice	Filtration after conventional press	Waste treatment
CO ₂ and excess air effluent	EtOH and P(3HB) fermentation	Waste treatment
Water-xylose purge	EtOH fermentation	Waste treatment
Cell and fermentation broth	P(3HB) fermentation	Waste treatment
Ethanol	EtOH fermentation	Product
P(3HB) bioplastic	P(3HB) fermentation	Product

The EP at this level is calculated as 39.27 M\$/y, after mass balance of the process is performed, as shown in Table 4. Note that the processing cost of raw material is based on the estimation reported by Zahari et al. (2015).

Table 4: Economic potential for Level 2

Product and byproduct cost	Cost (\$/t)	Amount produced (t/y)	Cost (\$/y) ^d
P(3HB)	2,000	17,635	35,270,000
Ethanol	666	17,428	11607,000
Raw material cost^a			
Water	1	1,263	2,000
Ammonia	310	191	60,000
Raw material processing cost			
Pre-processing ^b	5	300,000	1,500,000
Enzyme & catalyst	20	300,000	6,000,000
Waste disposal cost^c			
Solid residue	1	189	200
CO ₂ and excess air	1	19,179	20,000
Cell and fermentation broth	1	19,703	20,000
Xylose and water purge	1	269	300
Economic potential			39,275,000 (\$/y)
			39.27 (M\$/y)

^aRaw material cost of OPF is negligible as it is usually treated as waste which are left at harvesting site

^bThe cost estimate for pre-processing accounts for the reduction of moisture content, weight and volume preparation for specific end use such as chipping, drying, pelletising, shredding or compacting ranges from \$ 5-180/t for oil palm waste (Malaysian Innovation Agency, 2011). Note that drying accounts for a large proportion of the pre-processing cost. The fresh OPF utilised in the case study does not require drying. Hence, the pre-processing cost is estimated as \$5/t of OPF.

^cAssumption made for waste treatment/ disposal cost to be \$1/t

^d Cost rounded off to nearest thousand

Level 3: Recycle Structure of Flowsheet

For a OPF biorefinery, enzyme saccharification could be integrated with EtOH fermentation; this is known as *simultaneous saccharification and fermentation* (SSF), as shown in Figure 9.

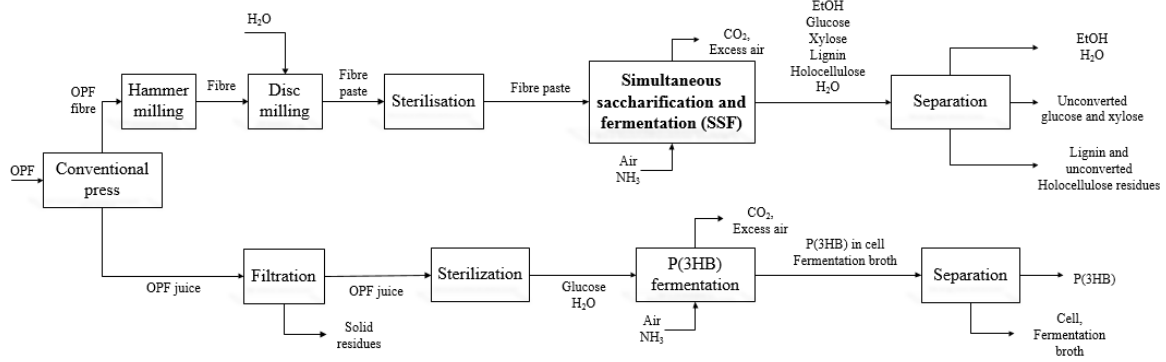


Figure 9. OPF biorefinery process with SSF alternative

However, this configuration is not selected as the technology for co-fermentation of glucose with xylose because it is still immature (Chen, 2010). Moreover, large proportion of glucose feed is sourced from OPF fibre rather than the OPF juice. Therefore, it is decided to separate the operations of saccharification and fermentation into individual distinct units. This allows the extraction of glucose from OPF fibre in saccharification, which can be converted to higher value-added bioplastics rather than bio-ethanol, as shown in Figure 10. Nevertheless, the SSF technology pathway can be treated as an alternative for future consideration when the technology become more mature. For both enzyme saccharification and EtOH fermentation, stirred batch fermenters with pH, temperature and air saturation adjustment are to be used. For P(3HB) fermenter, a fed-batch operation is selected to improve the productivity of bioplastic. It is reported that the cell dry weight and P(3HB) accumulation would be higher for fed-batch fermentation, due to the excess supply of carbon source for microbial growth and P(3HB) accumulation (Zahari et al., 2014).

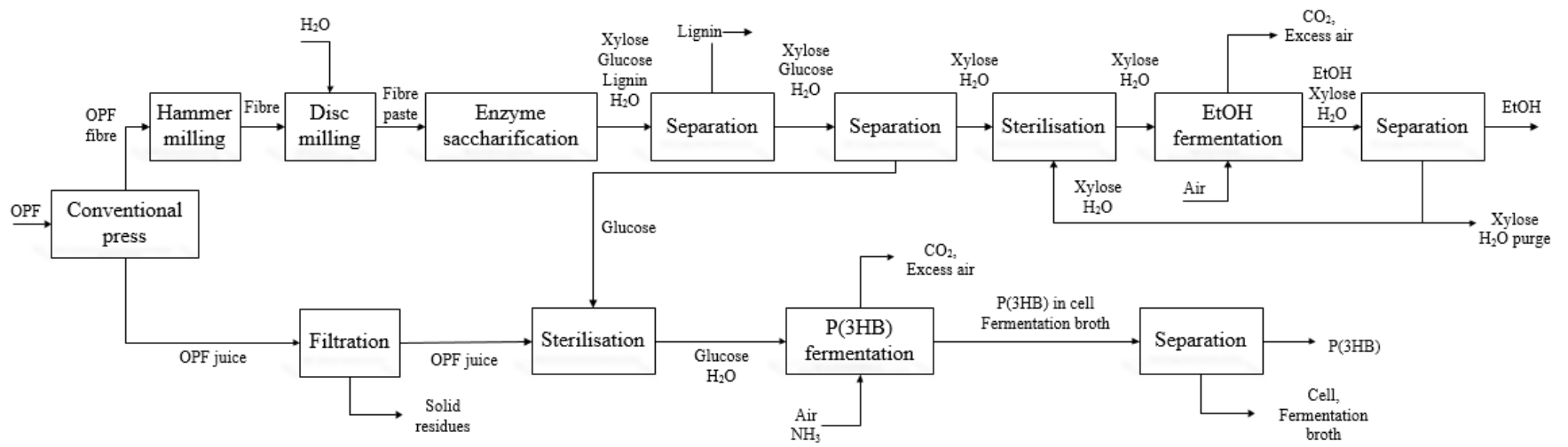


Figure 10. Recycle structure for OPF biorefinery process

The economic potential at this level reduces to 30.13 M\$/y, with the inclusion of cost calculations for the reaction systems. Note that no compressor cost is considered as no gaseous recycling is involved. From Table 5, it can be observed that P(3HB) fermenter contributes to a large portion of the purchased cost. This cost takes into account the large volume requirement of the P(3HB) fermenter due to its long residence time and reactant flow being continuously introduced into the fed-batch fermenter. The cost of enzyme saccharification fermenter is slightly more expensive than the EtOH fermenter as it handles a larger capacity of biomass, including lignin and holocellulose. In contrast, EtOH fermenter only handles xylose reactant stream to produce ethanol product. Therefore, possible research works could look into the feasibility of producing P(3HB) bioplastics in a continuous cultivation mode, as well as prior separation of lignin from holocellulose without incurring additional cost for processing.

Table 5: Economic potential for Level 3

Economic potential for Level 3	
Reactor and separators between reactors^a	Purchased cost (\$)
Enzyme saccharification fermenter	13,236,000
EtOH fermenter	9,369,000
P(3HB) fermenter	16,140,000
Total Installation cost ^b	56,180,000
Annualised reactor(s) and separation cost ^c	9,4926,000 \$/y
Annualised transfer cost ^d	-
Economic potential	30,130,000 \$/y
	30.13 M\$/y

^a Purchase cost of equipment were estimated in year 2017 using economic evaluation function of SuperPro Designer (Intelligen, 2005).

^b Installation cost of reactors is estimated using detailed factorial estimate with individual cost factors of equipment erection, piping, instrumentation, electrical and building (Sinnott, 2005)

^c The annualised cost is calculated with annual fractional interest rate of 5%, for a period of 15 years.

^d Recycling cost of xylose is not included as the liquid pumping cost is not high as compared to compressors or distillation units.

Level 4: Separation System

For this case study, solids and liquid phase split is required to separate the unconverted solid OPF fibre and lignin from liquid xylose and glucose after enzyme saccharification. Thus, filtration processes such as plate-and-frame can be used to remove fibre and lignin as dry cake. Besides, the solid cell containing P(3HB) plastics is to be separated from the P(3HB) fermentation effluent broth. Centrifugation can be used to separate the small cells from the aqueous fermentation medium. Compared to sedimentation and filtration, centrifugation offers the advantage of allowing faster separation in continuous mode.

We next move to single-phase separation. Note that no vapour recovery system is necessary, as the CO₂ and air stream from the fermenters are not being recycled as it does not contain any valuable products. On the other hand, liquid recovery system is designed to separate ethanol from xylose and water from the EtOH fermenter. Distillation is being employed to separate liquid mixtures consisting of components with different relative volatilities. Moreover, the presence of the high boiling point xylose could also serve as an extractive component to alter the relative volatility between water and ethanol and prevents the formation of water-ethanol azeotrope mixture. In addition, xylose and glucose solution from enzyme saccharification could also be separated by nanofiltration (Sjoman et al., 2007).

Solid recovery system is required to extract the solid, i.e. P(3HB) bio-plastics which is produced intracellularly by *C. necator* NCIMB 11599 bacteria. There are two well-established methods to recover bioplastics from cellular material, i.e. solvent extraction that dissolves the polymer, and chemical digestion which digests the non-polymer cellular material (NPCM) (Anis et al., 2012). Solvent extraction which is the most widely adopted method to recover bioplastics from the cell biomass involves the usage of organic solvent such as chloroform. Chloroform is first used to modify the cell membrane permeability to allow the release and solubilisation of P(3HB). A non-solvent methanol or ethanol is then used to precipitate the bioplastics. This method could obtain high purity and recovery of the P(3HB) plastics with high molecular weight. However, it uses large volume of volatile solvent which is hazardous. On the other hand, sodium hypochlorite is used in chemical digestion method to solubilise the NPCM. Therefore, solid P(3HB) can be separated from the cell and sodium hypochlorite solution by centrifugation. However, this method would reduce the bio-plastic molecular mass due to chemical degradation. Hence, many other methods are being innovated to avoid the use of non-environmental friendly solvent/chemicals that will degrade the polymer. Such examples are enzymatic digestion, mechanical cell disruption and usage of supercritical carbon dioxide solvent (Kunasundari and Sudesh, 2011). However, these methods are not suitable for large scale P(3HB) recovery as they are economically unattractive, and are still in the research phase.

In considering both economic and environmental factors, a suitable procedure for the recovery of bioplastics from bacterial cells is selected. The procedure makes use of cheap and environmental-friendly solvent (sodium hydroxide solution (NaOH)), which was reported by Mohammadi et al. (2012) and Anis et al. (2012). This method reports high

polymer recovery, with high yield of 87 wt%, and with little degradation of its molecular weight. Furthermore, organic solvent such as methanol, acetone or ethanol can be used to increase the product purity up to 90 wt%, by polishing the P(3HB) plastic pellets and rinsing out cell and solvent impurities (Mohammadi et al., 2012). Among the choice of organic solvent, ethanol is selected as the polishing solvent as it is environmentally benign, less volatile (as compared to methanol) and is able to remove grease and lipids of cell debris from the plastics. The subsequent solid-liquid separation between the solvent and bioplastics is carried out by centrifugation, as shown in the Figure 11.

The cost estimation for each separation units is critical as separation processes are usually energy intensive and accounts for a significant fraction of the total capital and operating costs. For this case, various developments have indicated that there is a potential for P(3HB) bioplastics to be the next generation source of plastics (Kunal and Anita, R., 2011). However, the current market penetration of P(3HB) bioplastics is still scare, due to its high production cost; the latter is mainly contributed by the costly fermentation and purification technologies. It is predicted that cost associated to bioplastic production would diminish only with further development of cheaper and environmental-friendly plastic recovery methods. Therefore, cheap and feasible separation methods, as well as alternative recovery system are essential to accelerate the success of this OPF biorefinery for bioplastic production (Ramaswamy et al., 2013). As shown in Table 6, the EP for Level 4 is reduced to 20.53 M\$.

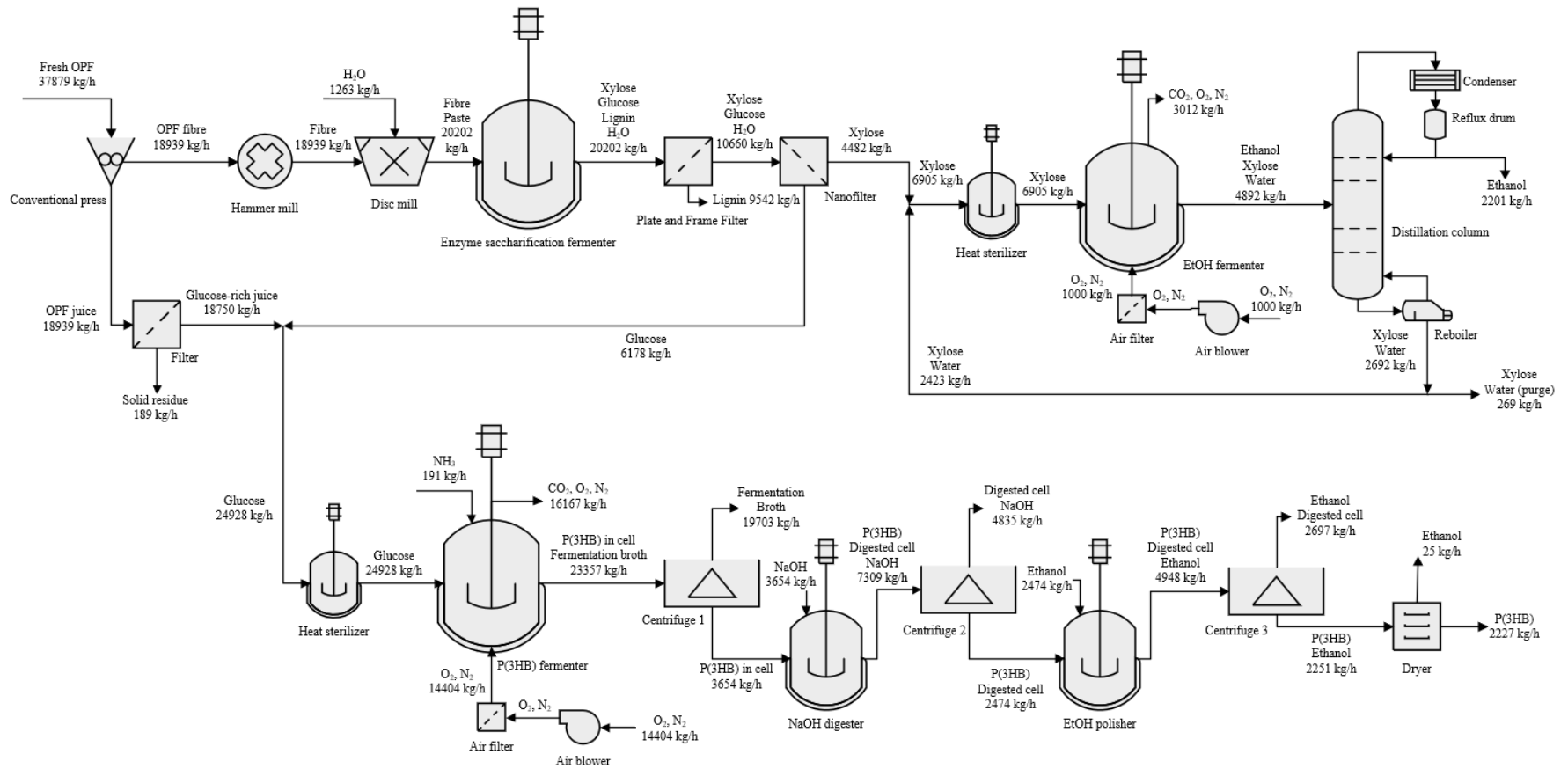


Figure 11. Separation system for OPF biorefinery

Table 6: Economic potential for Level 4

Separation system ^a	Purchased cost (\$)	Operating cost (\$/y)
Plate and frame filter	226,000	-
Nanofilter	115,000	-
Distillation column	64,000	2,869,000
Centrifuge 1	6,260,000	574,000
Centrifuge 2	1,260,000	61,000
Centrifuge 3	914,000	526,000
NaOH digester	1,230,000	4,200
EtOH polisher	905,000	2,637,000
Dryer	1449,000	1
Installation cost ^b	18,014,000	-
Annualised separation system cost ^c	30,436,000 \$/y	6,672,000 \$/y
Economic potential		20,525,000 \$/y
		20.53 MS/y

^a Purchase cost of equipment for separation system and their respective utility costs were estimated in year 2017 using economic evaluation function of SuperPro Designer, except that for nanofilter which cannot be simulated as an actual unit in the simulation. Its cost is calculated manually as shown in Appendix F.

^b Installation cost of reactors is estimated using detailed factorial estimate with individual cost factors of equipment erection, piping, instrumentation, electrical and building, described in Sinnott (2005)

^c The annualised cost is calculated with annual fractional interest rate of 5% and a period of 15 years.

Level 5: Task Integration

As mentioned earlier, the systematic methods for material recovery such as those for the recovery of water and solvent may be used to improve profitability of the process. Other than that, waste or by-products from the biorefinery process could also be utilised as other valuable products. For this case study, the residues of biomass from biorefinery facility can be retrieved for the generation of heat, steam and power supply (Sohel and Jack, 2011, Rabelo et al., 2011). CO₂-rich waste gases from biological conversion platforms can

also be used to generate useful products such as syngas, hydrogen, formic acid, methane, etc. (Sadhukhan et al., 2015). As a result, material integration is the key to unlock opportunities in synthesising a sustainable multi-product biorefinery. In cases where biomass (recovered from waste streams) has the potential to be utilised as product through the synthesis pathway, expansion to the existing biorefinery design can also be explored. For such cases, Level 0 can be revisited for the synthesis of the extended process.

Note that energy conservation and heat integration is an important element for a cost efficient biorefinery process. This is particularly true for biorefinery facility with highly exothermic thermochemical conversion pathways. A biofuel production process using hemicellulose from wood processing industry has demonstrated that heat integration could increase the economic potential of the process and improve its savings in utilities (Hossain et al., 2010). With regards to this, systematic method for energy conservation and heat integration are reported extensively in the literature (e.g. Douglas, 1985; Shenoy, 1995, Smith, 2016).

In this OPF case, auxiliary equipment are being added to the process. Material recovery was considered prior to heat integration, as waste solid biomass can be combusted for steam generation, in order to reduce the process utility requirements. Among the various waste streams of the process, dry OPF fibre cake from the filtration (after enzyme saccharification), which consists of lignin and unconverted holocellulose can be combusted for steam and electricity generation. However, for this OPF biorefinery which is mainly based on biological conversion platforms, heat integration and energy conservation may not be evidently necessary, as most process heating and cooling are carried out within the batch fermenters. Moreover, the biological process is operated at atmospheric conditions.

By proceeding with the process design through the six levels of the hierarchical decomposition approach, a feasible biorefinery process producing P(3HB) bioplastics and bioethanol from OPF is being designed. The process was simulated using commercial software, i.e. SuperPro Designer v.6 (www.inteligen.com), to ensure its validity. The simulation flowsheet is shown in Figure 12 (see Appendix G Supplementary Material in for its specification).

Finally, note that another biorefinery process using palm kernel shell as feedstock have also been synthesised using the extended procedure proposed in this work (see Supplementary Material for details).

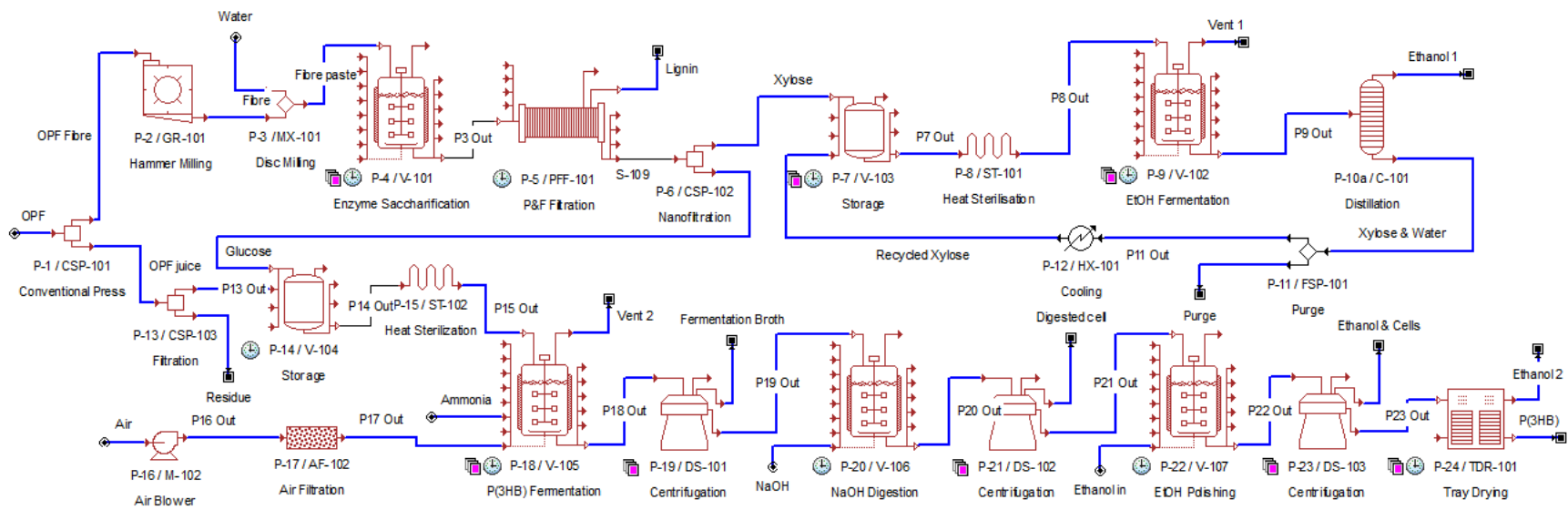


Figure 12. Simulation flowsheet of OPF biorefinery

CONCLUSION

The systematic hierarchical approach, i.e. Douglas's model has been improved and extended for the synthesis of biorefinery processes. Major modifications were carried out at Levels 0 and 2 to accommodate the limitations of the original hierarchical model in synthesising biorefinery processes. This extended approach provides three systematic steps to screen the conversion pathway and technologies at the early stage of process design. Challenges of biorefinery such as fluctuations and variation in feedstock supply are addressed through characterisation and feed purification tasks of the biomass. High processing cost for upstream feed purification and downstream separation are being evaluated with the economic potential calculations at Levels 2 and 4, respectively. Besides, individual reaction systems are being defined earlier within the input-output structure at Level 2. Doing this will ease mass balance calculation for the overall process, as some reaction pathways of biorefinery processes do not possess accurate reaction stoichiometry. Solid recovery system is considered at Level 4 for biorefinery which handles solid biomass/products. Other than that, improvement was made by considering material recovery and integration, which leads to reduced waste generation. A case study for the synthesis of biorefinery processes with palm-based biomass feedstock was used to demonstrate the proposed approach. Future work may consider simultaneous optimisation to be carried out at different levels of the hierarchical approach, where interactions exist.

SUPPLEMENTARY MATERIAL

Details of biomass characterisation is found in Appendix A. Appendices B – F are the supplementary materials for Example 1. Appendix G shows another example for the

synthesis of biorefinery from palm kernel shell, while the details of this example is shown in Appendix H.

NOTATION

BCI	biorefinery complexity index
CHP	combined heat and power generation
DOT	dissolved oxygen tension
EP	economic potential
EtOH	ethanol
FT	Fischer-Tropsch
H ₂ SO ₄	sulfuric acid
NaHSO ₃	sodium bisulphite
NaOH	sodium hydroxide
NH ₃	ammonia
OPF	oil palm frond
P(3HB)	(3-hydroxybutyrate) bio-plastic
PKS	palm kernel shell

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