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Abstract: In this study, a novel biorefinery concept producing carbon fibre-poly(butylene succinate) composite foam (CPC foam) from lignocellulose and CO₂ is modelled. The biodegradable nature of poly(butylene succinate) would allow for easy carbon fibre recovery from the CPC foam for reuse at the end of product lifecycle, thus allowing for a circular materials flow. Technical simulation results show the biorefinery consumes 417kg of biomass, 33kg of CO₂, 86kg of methanol, 23kg of acetic anhydride, 130kWh of electricity and 1,166kW of heat per hour. The facility generates 72kg of CPC foam, 82kg of carbon fibre, 24kg of tetrahydrofuran and 50kg of dimethyl ether (DME). DME is used to fulfil parasitic electricity requirement. These results demonstrate the technical viability of this biorefinery although, research is needed to reduce parasitic energy demand. This carbon negative biorefinery avoids carcinogens and halogens for polymeric materials synthesis by utilising green chemistry principles and lignocellulose feedstock.

20th June 2019

Professor Kai Sundmacher

Executive Editor, Chemical Engineering Science

Max Planck Institut, Magdeburg, Germany

RE: Submission of revised research paper

Dear Professor Kai Sundmacher

Please find the following revised research paper enclosed for your consideration:

Title: Modelling a biorefinery concept producing carbon fibre-polybutylene succinate composite foam

Corresponding author: Adeel Ghayur¹

Co-author: T. Vincent Verheyen¹

¹Carbon Technology Research Centre, Federation University Australia, Churchill, VIC 3842, Australia

We believe this revised manuscript is now suitable for publication in Chemical Engineering Science. The authors have incorporated the reviewer's helpful comment and rewrote the sentence avoiding the first person. A track-change version is provided as "RevMarked" file to assist your review of the change in the sentence.

If you require any further information, Adeel can be contacted by email (adeel.ghayur@federation.edu.au) or telephone +61 3 5122 6330.

We thank you for your time and consideration.

Best regards,

Adeel Ghayur

Response to the point raised by the reviewer of the following manuscript:

Paper Title: Modelling a biorefinery concept producing carbon fibre-polybutylene succinate composite foam

Author(s): Adeel Ghayur, T. Vincent Verheyen

Corresponding Author: Adeel Ghayur

Chemical Engineering Science

Manuscript ID: CES-D-19-00320

The authors wish to thank the reviewer for the constructive comment.

The point raised by the Reviewer is in the left column and Author response is provided in the right column.

Reviewer	
The sentence highlighted in red should be revised: "For the first time, our study explores this avenue via modelling the conversion of lignocellulose and CO2 into carbon fibre-poly(butylene succinate) composite foam (CPC foam). To the best of our knowledge, there is no published study in the area of technical modelling of a biorefinery producing carbon-fibre composite foam." - Please avoid the first person and re-write the sentence.	Thank you for your comment. The sentence on page#4 and line#17-20 has been rewritten, avoiding first person: For the first time, this study explores this avenue via modelling the conversion of lignocellulose and CO₂ into carbon fibre-poly(butylene succinate) composite foam (CPC foam).

*Highlights

- Technical simulation results of a carbon negative biorefinery are presented
- 417 kg of biomass and 33 kg of CO₂ are consumed per hour
- 72kg of recyclable carbon fibre-poly(butylene succinate) composite foam is produced
- The biorefinery also produces 82 kg/h of carbon fibre

Revised Marked Version

Modelling a biorefinery concept producing carbon fibre-polybutylene succinate composite foam

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Abstract

In this study, a novel biorefinery concept producing carbon fibre-poly(butylene succinate) composite foam (CPC foam) from lignocellulose and CO₂ is modelled. The biodegradable nature of poly(butylene succinate) would allow for easy carbon fibre recovery from the CPC foam for reuse at the end of product lifecycle, thus allowing for a circular materials flow. Technical simulation results show the biorefinery consumes 417kg of biomass, 33kg of CO₂, 86kg of methanol, 23kg of acetic anhydride, 130kWh of electricity and 1,166kW of heat per hour. The facility generates 72kg of CPC foam, 82kg of carbon fibre, 24kg of tetrahydrofuran and 50kg of dimethyl ether (DME). DME is used to fulfil parasitic electricity requirement. These results demonstrate the technical viability of this biorefinery although, research is needed to reduce parasitic energy demand. This carbon negative biorefinery avoids carcinogens and halogens for polymeric materials synthesis by utilising green chemistry principles and lignocellulose feedstock.

Keywords: biorefinery; circular economy; carbon negative; carbon fibre; simulation; succinic acid

1. Introduction

De-carbonisation of the world is paramount in view of the Intergovernmental Panel on Climate Change's latest report urging "rapid, far-reaching and unprecedented changes in all aspects of society," (IPCC, 2018) to keep temperature increase below 1.5 °C. Consequently, there is intense pressure on governments, industries and scientists to prioritise, invest and innovate for mitigating climate change, respectively. Substitution of fossil fuels with biomass for carbon based energy and products is one of the areas demanding further development via research and innovation such as carbon fibre products. Replacing metals with carbon fibre and its composites is of immense interest due to their high mechanical properties, low density, high temperature tolerance, low thermal expansion and thermal conductivity. Manufacturing a carbon fibre composite involves multiple processing steps of polymer production/extraction, its pretreatment, spinning, oxidative thermo-stabilisation, carbonisation and finally composite production.

Carbon fibres from the fossil fuel derived polymer polyacrylonitrile (PAN) are in highest demand due to superior physical, thermal and electrical properties. Over 90% of carbon fibres produced today employ PAN as a precursor, using wet- or dry-spinning (Liu and Kumar, 2012). However, toxic gases (e.g. cyanide) (Liu and Kumar, 2012), are emitted during carbon fibre manufacturing from PAN (Qu et al., 2018) and replacement low-cost, safer bio-precursors are being actively researched. Research on methods to refine the C3-methoxy phenolic polymer comprising lignin's matrix into carbon fibre were the subject of an early patent (Otani et al., 1969). These researchers evaluated several lignin-based precursors and methods including melt- and dry-spinning.

Lignin is a natural adhesive/binder and has some capacity to melt spin enabling this cost effective alternative to the wet spinning of PAN. PAN thermally decomposes below its melting temperature, making melt spinning impossible. In contrast to wet spinning, the melt spinning technique converts pure precursor directly into a fibre form at high process speeds and without the added expense of solvent recovery and recycling (Grassie and Hay, 1962). This makes melt spinning a preferred process

for producing low cost fibres for composites and structural applications (Baker and Rials, 2013; Meek et al., 2016). In this process the lignin is melted for extrusion through the spinneret and then directly solidified by cooling. The spinneret holes match the desired filament count of the carbon fibre (Chung, 1994).

Melt spinning requires lignin to be fusible (an ability to melt and flow), without undergoing extensive thermal-induced depolymerisation and/or condensation reactions during extrusion (Hosseinaei et al., 2017). Depolymerisation produces volatiles that lead to defects (mainly pores) on the surface of fibres, while condensation restricts lignin's thermal mobility and melt flow characteristics, consequently affecting spinning performance (Hosseinaei et al., 2017). Additionally, pores in the fibre lead to lower mechanical properties.

To ensure lignin fusibility, adequate pretreatment is required. In the 1990s, hydrogenated (Sudo and Shimizu, 1992); phenolated (Sudo et al., 1993) and acetylated (Uraki et al., 1995) lignins were investigated. Of these, acetylation gained traction due to its strengths. Thermal decomposition of acetylated lignin occurs at higher temperatures compared to non-acetylated lignin because acetylation hinders the cleavage of aryl ether linkages and other weaker bonds (Pu and Ragauskas, 2005). As discussed, this thermal stability is important as it determines the spinning performance of the precursor (Jiang et al., 2013) and ensures melt spinning is not interrupted by the formation of bubbles. Additionally, acetylated lignin could be processed via conventional plastic processing such as melt blending, extraction and injection moulding (Jeong et al., 2012).

After melt spinning, oxidative stabilisation and carbonisation is carried out to produce carbon fibres with a turbostratic carbon structure (Baker and Rials, 2013). Since lignin is already substantially oxidised, oxidative thermo-stabilisation of thermoplastic lignin fibre to thermoset lignin fibre proceeds more quickly (minutes) than for PAN (hours), which further reduces energy consumption (Baker and Rials, 2013). Another benefit of lignin over PAN is its capacity to produce a higher carbon fibre yield because of its relatively high carbon content (Qu et al., 2018). The resulting carbon fibre is

1 suitable for composite and composite foam production for wide ranging applications such as
2 insulation materials, sporting goods, biomedicine, automotive parts, maritime industry, textiles and
3 electronics.

4 The use of carbon fibre in the production of polymer composites for high-technology applications is
5 increasing rapidly on account of their good mechanical, thermal, and electrical properties (Liang et
6 al., 2014) and for engineering applications where weight-saving is of a major concern (Wong et al.,
7 2017) such as aerospace and wind energy industries. However, the biggest issue concerning carbon
8 fibre composites is handling of their waste at the end of product life. Aerospace is one of the
9 industries that is now grappled with this challenge (Wong et al., 2017). With the current focus on
10 Circular Economy models (Ghayur, 2019), it is imperative that these materials are reused to avoid
11 pollution and to reduce pressure on natural resources. Four recycling methods were recently
12 compared (Wong et al., 2017), all having considerable energy penalty. The main aim of all of these
13 processes is to use energy to separate out carbon fibre from the polymer matrix for reuse, however,
14 these processes degrade the quality of the carbon fibre. This is leading to research towards carbon
15 fibre/polymer composites made with biodegradable Poly(butylene succinate) (PBS) polymer (Han et
16 al., 2013; Liang et al., 2015; Kuang et al., 2018). This allows, in theory, biological separation of carbon
17 fibres from composites at end of product life, at very low cost with minimal degradation. For the first
18 time, this study explores this avenue via modelling the conversion of lignocellulose and CO₂ into
19 carbon fibre-poly(butylene succinate) composite foam (CPC foam). This novel biorefinery concept is
20 being modelled as a first step towards a pilot project for the Latrobe Valley of Victoria (Australia).
21 The Latrobe Valley has large forest and brown coal industries. These generate forest and CO₂ wastes
22 respectively, which are used as feedstock in the simulation of the biorefinery model. This synergetic
23 interaction between different industries in the Latrobe Valley allows for the investigation of this
24 biorefinery model as the part of a potential industrial ecosystem (Ghayur et al., 2019a; Ghayur and
25 Verheyen, 2018a). The main goals of this study are to investigate the technical parameters for a
26 biorefinery producing CPC foam to help identify future research areas towards improving the overall

design; model the biorefinery in such a manner that utilises all three lignocellulose components, thereby minimising waste generation; and design the concept enabling partial fulfilment of the energy and the chemical demands from biomass and CO₂.

2. Material and Methods

2.1 Methodology

The process simulation has been developed and carried out in COCO-ChemSep (version 7.21) simulation suite (COCO, 2018). The physical properties of the components were obtained either from its thermodynamic library or from NIST webbook (Mallard & Linstrom) via COCO-ChemSep's built-in import function. The simulation is done as a zero-dimensional energy model. Simulation parameters are listed in the process description in the next section. Since, this is the first time such a biorefinery concept has been developed, any assumptions required during process parameterisation, are outlined within the process description.

2.2 Facility Process Description

The biorefinery designed here is divided into six sections, namely: Pretreatment Area; Succinic Acid Area; PBS Area; Acetic Acid Area; Carbon Fibre Area and Foaming Area. All of these are described below.

Pretreatment Area (A100)

Sawdust is used as lignocellulose feedstock. It is conveyed to the disk mill and ground to 1 mm size. The milled biomass is sent for fractionation. This is a four-stepped process (Humbird et al., 2011). First, in a pre-steamer the solids enter at 30% weight (wt.) concentration and the temperature is kept above 100 °C for 10 minutes. Next, the slurry enters the screw extruder and the temperature is raised to just under 160 °C for five minutes. 18 kg of sulphuric acid per 1,000 kg of biomass is added. In the third step 4.1 kg of sulphuric acid per 1,000 kg of biomass is added and the temperature is

kept at 130 °C for 30 minutes. In the final step temperature is lowered to 75 °C for another 30 minutes. Slurry is then flash-cooled, vaporising 10% (wt.) of water. The extruded biomass is cooled in the wash tank and centrifuged into separate solid and liquid streams. Solid stream consists of cellulose, lignin, mineral/inorganics (ash) and 10% of hemicellulose, all with 30% moisture. Liquid stream containing 90% of the hemicellulose is sent to acetic acid digestion (A400). Solid stream is sent to De-Lignification. Here it is washed with ethanol-water-biomass (1:0.8:0.2 wt. ratio) solution to remove the lignin. The washing temperature is controlled at about 80 °C (Lv et al., 2013; Schulze et al., 2016). Solid cellulose is separated for succinic acid digestion (A200) while the lignin solution is sent for distillation. At 85 °C, ethanol is distilled out and recycled back. The process recovers 80% of the lignin which is dried and sent for acetylation (A500).

Succinic Acid Area (A200)

Separated cellulose, ash and the rest of the lignin from De-Lignification (A100) enter the hydrolysis tank where cellulase enzymes convert cellulose into glucose monomer ($(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$). Temperature is kept at 48 °C with a residence time of 48 hours. At the end, glucose with the rest of the slurry is sent to the digester. Here *Actinobacillus succinogenes* are used for glucose's conversion to succinic acid ($7C_6H_{12}O_6 + 6CO_2 \rightarrow 12C_4H_6O_4 + 6H_2O$). This bacterial species is capnophilic (CO₂ loving) requiring a CO₂ feed into the fermenter. Temperature is controlled at 37 °C (Pateraki et al., 2016) and residence time is 36 hours. Cellulose to succinic acid conversion rate is taken as 80%. Broth exiting the digester is cooled down to 2–4 °C which crystallises succinic acid (Luque et al., 2009; Li et al., 2010). The broth then undergoes centrifugation to separate out succinic acid crystals and leftover solids/sugars from the liquid waste. The solid stream at 30% moisture (wt.) is assumed to retain 90% of the succinic acid crystals. This solid stream is first heated to 165 °C to evaporate water and other organic contaminants (e.g. pyruvic acid, acetic acid, formic acid) from succinic acid (Ghayur and Verheyen, 2018a) and then to 235 °C to evaporate and separate out succinic acid. Succinic acid is then sent to the PBS Area (A300).

PBS Area (A300)

Direct esterification of succinic acid ($C_4H_6O_4$) with 1,4-butanediol (BDO) is the most common way to produce PBS ($C_4H_6O_4 + C_4H_{10}O_2 \rightarrow C_8H_{12}O_4 + 2H_2O$) (Jacquel et al., 2011). For this process, first two-thirds of succinic acid (69%) is converted to BDO, which then reacts with the rest of the succinic acid to produce PBS. Succinic acid to BDO itself is a two-stepped process. Succinic acid is first hydrogenated to gamma-butyrolactone ($C_4H_6O_4 + 2H_2 \rightarrow C_4H_6O_2 + 2H_2O$) followed by gamma-butyrolactone's hydrogenation to BDO and tetrahydrofuran (THF) ($2C_4H_6O_2 + 4H_2 \rightarrow C_4H_{10}O_2 + C_4H_8O + H_2O$) (Kang et al., 2015). The reaction parameters are 200 °C and 79 atm (Kang et al., 2016). In the simulation 90% conversion rate is modelled. The succinic acid and the BDO oligomers are then transesterified under vacuum to form a high molar mass PBS polymer with 90% conversion efficiency. Process temperature is 230 °C (Jacquel et al., 2011; Xu and Guo, 2010). PBS is then sent to the foaming area (A600).

Acetic Acid Area (A400)

Liquid stream from the wash tank centrifuge (A100) containing mostly hemicellulose enters the hydrolysis tank where it is converted to monosaccharides ($(C_5H_8O_4)_n + nH_2O \rightarrow nC_5H_{10}O_5$) by enzymes at 48 °C. After 48 hours the slurry is sent to the acetic acid digester. *Moorella thermoacetica* converts monosaccharides to acetic acid ($2C_5H_{10}O_5 + H_2O \rightarrow 5C_2H_4O_2 + H_2O$) (Ghayur and Verheyen, 2018b; Ghayur et al., 2019b). Digestion is maintained at 58 °C for 72 hours (Balasubramanian et al., 2001; Barker and Kamen, 1945; Ehsanipour et al., 2016). 90% of the hemicellulose is converted to acetic acid. The broth then undergoes centrifugation, separating out solids from the aqueous acetic acid. In the next step methanol is reacted with aqueous acetic acid in a reactive distillation process ($C_2H_4O_2 + CH_4O \rightarrow C_3H_6O_2 + H_2O$). Methyl acetate and water are generated. The reaction temperature of over 85 °C and pressure of 5 atm are taken (Tong et al., 2013; Tong et al., 2014). In the next column methyl acetate reacts with methanol to produce Dimethyl Ether (DME) and acetic acid ($C_3H_6O_2 + CH_4O \rightarrow C_2H_6O + C_2H_4O_2$). Reaction parameters are 120 °C temperature and 5 atm of

pressure (Akkaravathasinp et al., 2015; Hoyme and Holcomb, 2003; Prapainainar et al., 2014). Using ketene process acetic acid is then converted to acetic anhydride ($2\text{C}_2\text{H}_4\text{O}_2 \rightarrow \text{C}_4\text{H}_6\text{O}_3 + \text{H}_2\text{O}$) (Padmanabhan et al., 1968) at 400 °C under partial vacuum (Johann and Martin, 1938) with a conversion rate of 90% and sent to the Carbon Fibre Area (A500).

Carbon Fibre Area (A500)

Lignin from De-Lignification process (A100) is acetylated with 0.75ml/g (0.787g/g) acetic anhydride/lignin ratio for 1 hour (Qu et al., 2018) at 85 °C (Qu et al., 2018; Zhang and Ogale, 2014). Acetylated lignin is fed to a twin screw extruder, preheated to 130 °C and circulated within the extruder for five minutes prior to drawing of the fibre (Qu et al., 2018). Extruded fibre is then spun around the roller. The as-spun fibres are heated for stabilisation and then carbonised at 1,000 °C (Qu et al., 2018; Zhang and Ogale, 2014). In the model all the carbon in the acetylated lignin is carbonised.

Foaming Area (A600)

20% (wt.) carbon fibre is added to PBS (Kuang et al., 2018). The composition is heated to 100 °C at 177 atm with scCO_2 to reach saturation. Next, it is cooled to 53 °C and depressurised to atmospheric pressure to carryout foaming (Kuang et al., 2018), thus obtaining CPC foam with 10% (wt.) CO_2 getting trapped in the polymer matrix.

Figure 1: Biorefinery Process Flowsheet

3. Results and Discussion

The biorefinery was simulated as a facility consuming 10 metric tonnes per day (t/d) of sawdust (dry) feedstock to produce CPC foam. Local biomass source of sawdust waste with cellulose (37.47%), hemicellulose (23.83%), lignin (30.03%) and minerals/others (8.67%) composition was used. This composition is an average of the values given in the Commonwealth Scientific and Industrial Research Organisation's (CSIRO) studies (Dekker, 1987; Dekker et al., 1987) and has been used previously (Ghayur et al., 2019b; Ghayur and Verheyen, 2018a) as providing a better representation of the heterogeneous nature of sawdust waste in Victoria.

Technical model of the system has been simulated based on the parameters listed in the previous section and results are presented in the following table (1). Individual stream data and parameters are provided in the table (2).

Biorefinery Consumption	Biorefinery Production
-------------------------	------------------------

Feedstock	Rate	Product	Rate
Biomass	416.7 kg	THF	23.95 kg
CO ₂	33.44 kg	Carbon Fibre	81.55 kg
Methanol	86.25 kg	CPC Foam	71.69 kg
Acetic Anhydride	22.55 kg	DME	50.23 kg
H ₂	5.38 kg	Electricity (DME)	185 kWh
Electricity	130.33 kWh		
Heat	1165.76 kW		

Table 1: Hourly Consumption and Production Rates

Stream#	s100	s101	s102	s103	s104	s105	s106	s107	s108
T (°C)	25	25	25	25	85	25	25	75	80
P (atm)	1	1	1.5	1.5	1.5	1.5	1.5	1.5	2
M (kg/h)	595.24	595.24	785.53	7.5	1388.27	816.78	467.58	2948.49	2805.49
Stream#	s109	s110	s111	s200	s201	s202	s203	s300	s301
T (°C)	80	25	25	25	37	25	235	25	25
P (atm)	2	1	1.5	1.5	1.5	1.5	1.5	1.5	80
M (kg/h)	143	100.1	324.58	26.27	1647.78	272.46	126.31	39.16	87.16
Stream#	s302	s303	s304	s400	s401	s402	s403	s404	s405
T (°C)	25	25	25	58	25	25	25	25	25
P (atm)	1.5	1.5	1	1.5	1.5	1.5	1.5	1.5	1.5
M (kg/h)	23.95	30.07	51.61	817.18	804.42	43.12	89.73	43.12	50.23
Stream#	s406	s407	s500	s501	s502	s503	s504	s600	s601
T (°C)	25	25	25	85	25	25	25	25	25
P (atm)	1.5	1.5	1.5	1.5	1.5	1	1	177	1
M (kg/h)	73.55	56.27	22.55	178.91	178.91	81.55	12.9	7.17	71.69

Table 2: Stream Data and Parameters

The biorefinery consumes 416.7 kg of biomass, 33.44 kg of CO₂, 86.25 kg of methanol, 22.55 kg of acetic anhydride, 130.33 kWh of electricity and 1165.76 kW of heat per hour. As a result, the simulated facility generates 71.69 kg of CPC foam, 81.55 kg of carbon fibre and 23.95 kg of THF. The facility also generates 50.23 kg of DME, enough to generate 185 kWh of electricity via a 50% efficient SOFC.

The CPC foam composite comprises only 20% (wt.) of carbon fibre as higher levels lead to agglomeration, thus weakening the composite (Liang et al., 2015). This is due to carbon fibre's dispersion becoming indisposed in the PBS matrix (Qu et al., 2011). Agglomeration could lead to inefficient stress transfer and the formation of stress concentrated region where less energy is required for promoting the crack propagation, resulting in a quicker fracture than that of either neat PBS or CPC foam (with lower carbon fibre proportion) (Qu et al., 2011).

To ensure a circular materials flow chain, the biodegradable polymer PBS is used thereby allowing for easier separation and reutilisation of carbon fibres at the end of the product lifecycle. Biodegradable aliphatic polyesters such as poly(3-hydroxybutyrate), poly(ϵ -caprolactone) and PBS are considered to be the most promising biodegradable plastics due to their high performance and environment friendliness (Shih and Chieh, 2007). Compared to other aliphatic polyesters PBS has: 1) excellent biocompatibility by bacteria and fungi (Wan and Chen, 2013; Kim and Rhee, 2003); 2) desirable properties including melt processability, thermal and chemical resistance; 3) high Technology Readiness Level for biosynthesis; and 4) established commercial application in a myriad of industries such as biomedical field, agricultural films, disposables, packaging materials, and foaming products. These properties allow PBS based CPC foam to have application in a wide range of areas such as electronic equipment e.g. mobile phone cases, sports e.g. golf nail, garments e.g. inner liner of shoes, fishing e.g. fish lures and so forth.

Results show biorefinery's total carbon fibre production stands at 94.46 kg/h of which 12.9 kg/h is consumed in the CPC foam production, leaving behind a large fraction (81.55 kg/h). Although, lignin-based carbon fibre currently does not compete with PAN-based carbon fibre for structural applications (Ghayan, 2018a), it is still considered suitable for many general applications. These include areas where materials with moderately high mechanical properties, low density, high temperature tolerance, low thermal expansion, and thermal conductivity are of interest (Qu et al., 2018). For example, high-temperature-tolerant insulation products, sporting goods like tennis racquets and bicycles, garments like motorcycle gloves, and other applications discussed earlier.

In this study lignin was acetylated using acetic anhydride in the presence of a catalyst. Other scientists have investigated acetylation of lignin using acetic anhydride (Jeong et al., 2012), scCO_2 (Cachet et al., 2014) and microwaves (Monteil-Rivera and Paquet, 2015). Acetylation under scCO_2 environment is a promising process as it is catalyst free and uses lower temperature. However, currently its acetic anhydride requirements are quite high. Its future depends upon the reduction of the acetic anhydride quantity utilised during the process.

The biorefinery model produces 73.55 kg/h of acetic acid, which is converted to 56.27 kg/h of acetic anhydride and consumed during acetylation. An additional 22.55 kg/h of acetic anhydride is needed to fulfil the acetylation demand. However, due to higher molecular weight of the lignin and the amount of accessible phenolic hydroxyls i.e. free hydroxyl groups, the total amount of acetic anhydride used should be much less and lower still if partial acetylation is intended. Thus, there is much scope to improve this process and considerably reduce the acetic anhydride demand. For a commercial biorefinery, this would be important to ensure economic competitiveness.

The biorefinery produces 126.31 kg/h of succinic acid which produces 51.61 kg/h of PBS all of which is consumed for the generation of CPC foam. This process generates a significant quantity of THF as a by-product. THF has application as a solvent and primarily used as a precursor for polymers such as spandex (Pruckmayr et al., 1996).

1 The biorefinery consumes 26.27 kg/h and 7.17 kg/h of CO₂ in the succinic acid production and
2 foaming processes. There is CO₂ present in the headspace of the acetic acid digester, however, it is
3 marginally consumed within the process. The presence of this CO₂ forces the *Moorella*
4 *thermoacetica* to utilise all the CO₂ that is produced during the digestion process, thereby achieving
5 higher conversion rates.

6 In the simulation DME is used in the SOFC with 50% efficiency. Published research shows the
7 promise of DME as a suitable fuel for SOFC (Murray et al., 2002; Su et al., 2011). The issue with DME
8 as a fuel for SOFC is similar to that of any other hydrocarbon fuel. It leads to coking.

9 Further breakdowns of heat and electricity demands are provided in the figures (2) and (3)
10 respectively. Pretreatment Area (A100) consumes the most heat, nearly 80% of the total demand.
11 This is due to the presence of large water content in the three main processes of fractionation, de-
12 lignification and lignin drier consuming 745.83 kW, 181 kW and 16.22 kW respectively. Research is
13 needed to develop newer processes for biomass fractionation that operate at lower temperatures
14 and/or with much less water. Carbon Fibre Area (A500) has the second highest heat duty due to the
15 carbonisation process consuming 78.53 kW of energy.

16 The large parasitic heat demand shows there is much room for improvement. This involves
17 optimisation research on energy consumption of individual processes and re-design of the overall
18 concept to incorporate alternatives with lower energy demand.

Figure 2: Hourly Heat Duty Breakdown (1165.76 kW)

Figure 3: Hourly Electricity Demand Breakdown (130.33 kWh)

Another option to consider is re-design of the biorefinery in such a manner that allows for some of the lignin to be combusted for energy generation. However, this would reduce the carbon fibre

production and detailed economic assessment would be needed for a comparison of the two models. A part of this research would entail 3- and 4-dimensional modelling of the facility for detailed investigation of the technical data.

Lastly, while the simulation results are promising and show the technical viability of a biorefinery producing biodegradable carbon fibre composite, research is still needed to optimise the reuse of the carbon fibre from the end-of-life products. One area of research is the separation of carbon fibres in usable form from the PBS matrix via biodegradation. Only then, closed materials supply chain for a circular economy (Ghayan, 2018b) can be established.

4. Conclusion

In this study a novel biorefinery model converting sawdust waste and CO₂ into carbon fibre-poly(butylene succinate) foam (CPC foam) was simulated. Results show that the biorefinery consumes 417 kg of biomass, 33 kg of CO₂, 86 kg of methanol, 23 kg of acetic anhydride, 130 kW of electricity and 1,166 kW of heat per hour. Its main products are 72 kg of CPC foam and 82 kg of carbon fibre. The facility also generates 24 kg of THF as a by-product. 50 kg of DME is produced as a side-product during the reactive distillation of acetic acid and is enough to fulfil parasitic electricity requirement of the biorefinery. A large heat demand is a major hurdle and research is needed towards its reduction. Biomass fractionation into cellulose, hemicellulose and lignin consumes the most heat, 80% of the total biorefinery demand, mainly due to the high water content in the process. There is a need to develop biomass fractionation processes that either require less water or utilise less energy intensive technologies. A continuing area of research is biological separation of the polymer from the carbon fibres and their reuse. Despite these unanswered research questions, simulation results show promise for biodegradable carbon fibre composites from lignocellulose and CO₂ playing a role in closed materials supply chain, thereby helping in the transition of linear economies to circular economies.

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Modelling a biorefinery concept producing carbon fibre-polybutylene succinate composite foam

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Abstract

In this study, a novel biorefinery concept producing carbon fibre-poly(butylene succinate) composite foam (CPC foam) from lignocellulose and CO₂ is modelled. The biodegradable nature of poly(butylene succinate) would allow for easy carbon fibre recovery from the CPC foam for reuse at the end of product lifecycle, thus allowing for a circular materials flow. Technical simulation results show the biorefinery consumes 417kg of biomass, 33kg of CO₂, 86kg of methanol, 23kg of acetic anhydride, 130kWh of electricity and 1,166kW of heat per hour. The facility generates 72kg of CPC foam, 82kg of carbon fibre, 24kg of tetrahydrofuran and 50kg of dimethyl ether (DME). DME is used to fulfil parasitic electricity requirement. These results demonstrate the technical viability of this biorefinery although, research is needed to reduce parasitic energy demand. This carbon negative biorefinery avoids carcinogens and halogens for polymeric materials synthesis by utilising green chemistry principles and lignocellulose feedstock.

Keywords: biorefinery; circular economy; carbon negative; carbon fibre; simulation; succinic acid

1. Introduction

De-carbonisation of the world is paramount in view of the Intergovernmental Panel on Climate Change's latest report urging "rapid, far-reaching and unprecedented changes in all aspects of society," (IPCC, 2018) to keep temperature increase below 1.5 °C. Consequently, there is intense pressure on governments, industries and scientists to prioritise, invest and innovate for mitigating climate change, respectively. Substitution of fossil fuels with biomass for carbon based energy and products is one of the areas demanding further development via research and innovation such as carbon fibre products. Replacing metals with carbon fibre and its composites is of immense interest due to their high mechanical properties, low density, high temperature tolerance, low thermal expansion and thermal conductivity. Manufacturing a carbon fibre composite involves multiple processing steps of polymer production/extraction, its pretreatment, spinning, oxidative thermo-stabilisation, carbonisation and finally composite production.

Carbon fibres from the fossil fuel derived polymer polyacrylonitrile (PAN) are in highest demand due to superior physical, thermal and electrical properties. Over 90% of carbon fibres produced today employ PAN as a precursor, using wet- or dry-spinning (Liu and Kumar, 2012). However, toxic gases (e.g. cyanide) (Liu and Kumar, 2012), are emitted during carbon fibre manufacturing from PAN (Qu et al., 2018) and replacement low-cost, safer bio-precursors are being actively researched. Research on methods to refine the C3-methoxy phenolic polymer comprising lignin's matrix into carbon fibre were the subject of an early patent (Otani et al., 1969). These researchers evaluated several lignin-based precursors and methods including melt- and dry-spinning.

Lignin is a natural adhesive/binder and has some capacity to melt spin enabling this cost effective alternative to the wet spinning of PAN. PAN thermally decomposes below its melting temperature, making melt spinning impossible. In contrast to wet spinning, the melt spinning technique converts pure precursor directly into a fibre form at high process speeds and without the added expense of solvent recovery and recycling (Grassie and Hay, 1962). This makes melt spinning a preferred process

for producing low cost fibres for composites and structural applications (Baker and Rials, 2013; Meek et al., 2016). In this process the lignin is melted for extrusion through the spinneret and then directly solidified by cooling. The spinneret holes match the desired filament count of the carbon fibre (Chung, 1994).

Melt spinning requires lignin to be fusible (an ability to melt and flow), without undergoing extensive thermal-induced depolymerisation and/or condensation reactions during extrusion (Hosseinaei et al., 2017). Depolymerisation produces volatiles that lead to defects (mainly pores) on the surface of fibres, while condensation restricts lignin's thermal mobility and melt flow characteristics, consequently affecting spinning performance (Hosseinaei et al., 2017). Additionally, pores in the fibre lead to lower mechanical properties.

To ensure lignin fusibility, adequate pretreatment is required. In the 1990s, hydrogenated (Sudo and Shimizu, 1992); phenolated (Sudo et al., 1993) and acetylated (Uraki et al., 1995) lignins were investigated. Of these, acetylation gained traction due to its strengths. Thermal decomposition of acetylated lignin occurs at higher temperatures compared to non-acetylated lignin because acetylation hinders the cleavage of aryl ether linkages and other weaker bonds (Pu and Ragauskas, 2005). As discussed, this thermal stability is important as it determines the spinning performance of the precursor (Jiang et al., 2013) and ensures melt spinning is not interrupted by the formation of bubbles. Additionally, acetylated lignin could be processed via conventional plastic processing such as melt blending, extraction and injection moulding (Jeong et al., 2012).

After melt spinning, oxidative stabilisation and carbonisation is carried out to produce carbon fibres with a turbostratic carbon structure (Baker and Rials, 2013). Since lignin is already substantially oxidised, oxidative thermo-stabilisation of thermoplastic lignin fibre to thermoset lignin fibre proceeds more quickly (minutes) than for PAN (hours), which further reduces energy consumption (Baker and Rials, 2013). Another benefit of lignin over PAN is its capacity to produce a higher carbon fibre yield because of its relatively high carbon content (Qu et al., 2018). The resulting carbon fibre is

1 suitable for composite and composite foam production for wide ranging applications such as
2 insulation materials, sporting goods, biomedicine, automotive parts, maritime industry, textiles and
3 electronics.

4 The use of carbon fibre in the production of polymer composites for high-technology applications is
5 increasing rapidly on account of their good mechanical, thermal, and electrical properties (Liang et
6 al., 2014) and for engineering applications where weight-saving is of a major concern (Wong et al.,
7 2017) such as aerospace and wind energy industries. However, the biggest issue concerning carbon
8 fibre composites is handling of their waste at the end of product life. Aerospace is one of the
9 industries that is now grappled with this challenge (Wong et al., 2017). With the current focus on
10 Circular Economy models (Ghayur, 2019), it is imperative that these materials are reused to avoid
11 pollution and to reduce pressure on natural resources. Four recycling methods were recently
12 compared (Wong et al., 2017), all having considerable energy penalty. The main aim of all of these
13 processes is to use energy to separate out carbon fibre from the polymer matrix for reuse, however,
14 these processes degrade the quality of the carbon fibre. This is leading to research towards carbon
15 fibre/polymer composites made with biodegradable Poly(butylene succinate) (PBS) polymer (Han et
16 al., 2013; Liang et al., 2015; Kuang et al., 2018). This allows, in theory, biological separation of carbon
17 fibres from composites at end of product life, at very low cost with minimal degradation. For the first
18 time, this study explores this avenue via modelling the conversion of lignocellulose and CO₂ into
19 carbon fibre-poly(butylene succinate) composite foam (CPC foam). This novel biorefinery concept is
20 being modelled as a first step towards a pilot project for the Latrobe Valley of Victoria (Australia).
21 The Latrobe Valley has large forest and brown coal industries. These generate forest and CO₂ wastes
22 respectively, which are used as feedstock in the simulation of the biorefinery model. This synergetic
23 interaction between different industries in the Latrobe Valley allows for the investigation of this
24 biorefinery model as the part of a potential industrial ecosystem (Ghayur et al., 2019a; Ghayur and
25 Verheyen, 2018a). The main goals of this study are to investigate the technical parameters for a
26 biorefinery producing CPC foam to help identify future research areas towards improving the overall

design; model the biorefinery in such a manner that utilises all three lignocellulose components, thereby minimising waste generation; and design the concept enabling partial fulfilment of the energy and the chemical demands from biomass and CO₂.

2. Material and Methods

2.1 Methodology

The process simulation has been developed and carried out in COCO-ChemSep (version 7.21) simulation suite (COCO, 2018). The physical properties of the components were obtained either from its thermodynamic library or from NIST webbook (Mallard & Linstrom) via COCO-ChemSep's built-in import function. The simulation is done as a zero-dimensional energy model. Simulation parameters are listed in the process description in the next section. Since, this is the first time such a biorefinery concept has been developed, any assumptions required during process parameterisation, are outlined within the process description.

2.2 Facility Process Description

The biorefinery designed here is divided into six sections, namely: Pretreatment Area; Succinic Acid Area; PBS Area; Acetic Acid Area; Carbon Fibre Area and Foaming Area. All of these are described below.

Pretreatment Area (A100)

Sawdust is used as lignocellulose feedstock. It is conveyed to the disk mill and ground to 1 mm size. The milled biomass is sent for fractionation. This is a four-stepped process (Humbird et al., 2011). First, in a pre-steamer the solids enter at 30% weight (wt.) concentration and the temperature is kept above 100 °C for 10 minutes. Next, the slurry enters the screw extruder and the temperature is raised to just under 160 °C for five minutes. 18 kg of sulphuric acid per 1,000 kg of biomass is added. In the third step 4.1 kg of sulphuric acid per 1,000 kg of biomass is added and the temperature is

kept at 130 °C for 30 minutes. In the final step temperature is lowered to 75 °C for another 30 minutes. Slurry is then flash-cooled, vaporising 10% (wt.) of water. The extruded biomass is cooled in the wash tank and centrifuged into separate solid and liquid streams. Solid stream consists of cellulose, lignin, mineral/inorganics (ash) and 10% of hemicellulose, all with 30% moisture. Liquid stream containing 90% of the hemicellulose is sent to acetic acid digestion (A400). Solid stream is sent to De-Lignification. Here it is washed with ethanol-water-biomass (1:0.8:0.2 wt. ratio) solution to remove the lignin. The washing temperature is controlled at about 80 °C (Lv et al., 2013; Schulze et al., 2016). Solid cellulose is separated for succinic acid digestion (A200) while the lignin solution is sent for distillation. At 85 °C, ethanol is distilled out and recycled back. The process recovers 80% of the lignin which is dried and sent for acetylation (A500).

Succinic Acid Area (A200)

Separated cellulose, ash and the rest of the lignin from De-Lignification (A100) enter the hydrolysis tank where cellulase enzymes convert cellulose into glucose monomer ($(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$). Temperature is kept at 48 °C with a residence time of 48 hours. At the end, glucose with the rest of the slurry is sent to the digester. Here *Actinobacillus succinogenes* are used for glucose's conversion to succinic acid ($7C_6H_{12}O_6 + 6CO_2 \rightarrow 12C_4H_6O_4 + 6H_2O$). This bacterial species is capnophilic (CO₂ loving) requiring a CO₂ feed into the fermenter. Temperature is controlled at 37 °C (Pateraki et al., 2016) and residence time is 36 hours. Cellulose to succinic acid conversion rate is taken as 80%. Broth exiting the digester is cooled down to 2–4 °C which crystallises succinic acid (Luque et al., 2009; Li et al., 2010). The broth then undergoes centrifugation to separate out succinic acid crystals and leftover solids/sugars from the liquid waste. The solid stream at 30% moisture (wt.) is assumed to retain 90% of the succinic acid crystals. This solid stream is first heated to 165 °C to evaporate water and other organic contaminants (e.g. pyruvic acid, acetic acid, formic acid) from succinic acid (Ghayur and Verheyen, 2018a) and then to 235 °C to evaporate and separate out succinic acid. Succinic acid is then sent to the PBS Area (A300).

PBS Area (A300)

Direct esterification of succinic acid ($C_4H_6O_4$) with 1,4-butanediol (BDO) is the most common way to produce PBS ($C_4H_6O_4 + C_4H_{10}O_2 \rightarrow C_8H_{12}O_4 + 2H_2O$) (Jacquel et al., 2011). For this process, first two-thirds of succinic acid (69%) is converted to BDO, which then reacts with the rest of the succinic acid to produce PBS. Succinic acid to BDO itself is a two-stepped process. Succinic acid is first hydrogenated to gamma-butyrolactone ($C_4H_6O_4 + 2H_2 \rightarrow C_4H_6O_2 + 2H_2O$) followed by gamma-butyrolactone's hydrogenation to BDO and tetrahydrofuran (THF) ($2C_4H_6O_2 + 4H_2 \rightarrow C_4H_{10}O_2 + C_4H_8O + H_2O$) (Kang et al., 2015). The reaction parameters are 200 °C and 79 atm (Kang et al., 2016). In the simulation 90% conversion rate is modelled. The succinic acid and the BDO oligomers are then transesterified under vacuum to form a high molar mass PBS polymer with 90% conversion efficiency. Process temperature is 230 °C (Jacquel et al., 2011; Xu and Guo, 2010). PBS is then sent to the foaming area (A600).

Acetic Acid Area (A400)

Liquid stream from the wash tank centrifuge (A100) containing mostly hemicellulose enters the hydrolysis tank where it is converted to monosaccharides ($(C_5H_8O_4)_n + nH_2O \rightarrow nC_5H_{10}O_5$) by enzymes at 48 °C. After 48 hours the slurry is sent to the acetic acid digester. *Moorella thermoacetica* converts monosaccharides to acetic acid ($2C_5H_{10}O_5 + H_2O \rightarrow 5C_2H_4O_2 + H_2O$) (Ghayur and Verheyen, 2018b; Ghayur et al., 2019b). Digestion is maintained at 58 °C for 72 hours (Balasubramanian et al., 2001; Barker and Kamen, 1945; Ehsanipour et al., 2016). 90% of the hemicellulose is converted to acetic acid. The broth then undergoes centrifugation, separating out solids from the aqueous acetic acid. In the next step methanol is reacted with aqueous acetic acid in a reactive distillation process ($C_2H_4O_2 + CH_4O \rightarrow C_3H_6O_2 + H_2O$). Methyl acetate and water are generated. The reaction temperature of over 85 °C and pressure of 5 atm are taken (Tong et al., 2013; Tong et al., 2014). In the next column methyl acetate reacts with methanol to produce Dimethyl Ether (DME) and acetic acid ($C_3H_6O_2 + CH_4O \rightarrow C_2H_6O + C_2H_4O_2$). Reaction parameters are 120 °C temperature and 5 atm of

pressure (Akkaravathasinp et al., 2015; Hoyme and Holcomb, 2003; Prapainainar et al., 2014). Using ketene process acetic acid is then converted to acetic anhydride ($2\text{C}_2\text{H}_4\text{O}_2 \rightarrow \text{C}_4\text{H}_6\text{O}_3 + \text{H}_2\text{O}$) (Padmanabhan et al., 1968) at 400 °C under partial vacuum (Johann and Martin, 1938) with a conversion rate of 90% and sent to the Carbon Fibre Area (A500).

Carbon Fibre Area (A500)

Lignin from De-Lignification process (A100) is acetylated with 0.75ml/g (0.787g/g) acetic anhydride/lignin ratio for 1 hour (Qu et al., 2018) at 85 °C (Qu et al., 2018; Zhang and Ogale, 2014). Acetylated lignin is fed to a twin screw extruder, preheated to 130 °C and circulated within the extruder for five minutes prior to drawing of the fibre (Qu et al., 2018). Extruded fibre is then spun around the roller. The as-spun fibres are heated for stabilisation and then carbonised at 1,000 °C (Qu et al., 2018; Zhang and Ogale, 2014). In the model all the carbon in the acetylated lignin is carbonised.

Foaming Area (A600)

20% (wt.) carbon fibre is added to PBS (Kuang et al., 2018). The composition is heated to 100 °C at 177 atm with scCO_2 to reach saturation. Next, it is cooled to 53 °C and depressurised to atmospheric pressure to carryout foaming (Kuang et al., 2018), thus obtaining CPC foam with 10% (wt.) CO_2 getting trapped in the polymer matrix.

Feedstock	Rate	Product	Rate
Biomass	416.7 kg	THF	23.95 kg
CO ₂	33.44 kg	Carbon Fibre	81.55 kg
Methanol	86.25 kg	CPC Foam	71.69 kg
Acetic Anhydride	22.55 kg	DME	50.23 kg
H ₂	5.38 kg	Electricity (DME)	185 kWh
Electricity	130.33 kWh		
Heat	1165.76 kW		

1

Table 1: Hourly Consumption and Production Rates

2

Stream#	s100	s101	s102	s103	s104	s105	s106	s107	s108
T (°C)	25	25	25	25	85	25	25	75	80
P (atm)	1	1	1.5	1.5	1.5	1.5	1.5	1.5	2
M (kg/h)	595.24	595.24	785.53	7.5	1388.27	816.78	467.58	2948.49	2805.49
Stream#	s109	s110	s111	s200	s201	s202	s203	s300	s301
T (°C)	80	25	25	25	37	25	235	25	25
P (atm)	2	1	1.5	1.5	1.5	1.5	1.5	1.5	80
M (kg/h)	143	100.1	324.58	26.27	1647.78	272.46	126.31	39.16	87.16
Stream#	s302	s303	s304	s400	s401	s402	s403	s404	s405
T (°C)	25	25	25	58	25	25	25	25	25
P (atm)	1.5	1.5	1	1.5	1.5	1.5	1.5	1.5	1.5
M (kg/h)	23.95	30.07	51.61	817.18	804.42	43.12	89.73	43.12	50.23
Stream#	s406	s407	s500	s501	s502	s503	s504	s600	s601
T (°C)	25	25	25	85	25	25	25	25	25
P (atm)	1.5	1.5	1.5	1.5	1.5	1	1	177	1
M (kg/h)	73.55	56.27	22.55	178.91	178.91	81.55	12.9	7.17	71.69

Table 2: Stream Data and Parameters

The biorefinery consumes 416.7 kg of biomass, 33.44 kg of CO₂, 86.25 kg of methanol, 22.55 kg of acetic anhydride, 130.33 kWh of electricity and 1165.76 kW of heat per hour. As a result, the simulated facility generates 71.69 kg of CPC foam, 81.55 kg of carbon fibre and 23.95 kg of THF. The facility also generates 50.23 kg of DME, enough to generate 185 kWh of electricity via a 50% efficient SOFC.

The CPC foam composite comprises only 20% (wt.) of carbon fibre as higher levels lead to agglomeration, thus weakening the composite (Liang et al., 2015). This is due to carbon fibre's dispersion becoming indisposed in the PBS matrix (Qu et al., 2011). Agglomeration could lead to inefficient stress transfer and the formation of stress concentrated region where less energy is required for promoting the crack propagation, resulting in a quicker fracture than that of either neat PBS or CPC foam (with lower carbon fibre proportion) (Qu et al., 2011).

To ensure a circular materials flow chain, the biodegradable polymer PBS is used thereby allowing for easier separation and reutilisation of carbon fibres at the end of the product lifecycle. Biodegradable aliphatic polyesters such as poly(3-hydroxybutyrate), poly(ϵ -caprolactone) and PBS are considered to be the most promising biodegradable plastics due to their high performance and environment friendliness (Shih and Chieh, 2007). Compared to other aliphatic polyesters PBS has: 1) excellent biocompatibility by bacteria and fungi (Wan and Chen, 2013; Kim and Rhee, 2003); 2) desirable properties including melt processability, thermal and chemical resistance; 3) high Technology Readiness Level for biosynthesis; and 4) established commercial application in a myriad of industries such as biomedical field, agricultural films, disposables, packaging materials, and foaming products. These properties allow PBS based CPC foam to have application in a wide range of areas such as electronic equipment e.g. mobile phone cases, sports e.g. golf nail, garments e.g. inner liner of shoes, fishing e.g. fish lures and so forth.

Results show biorefinery's total carbon fibre production stands at 94.46 kg/h of which 12.9 kg/h is consumed in the CPC foam production, leaving behind a large fraction (81.55 kg/h). Although, lignin-based carbon fibre currently does not compete with PAN-based carbon fibre for structural applications (Ghayan, 2018a), it is still considered suitable for many general applications. These include areas where materials with moderately high mechanical properties, low density, high temperature tolerance, low thermal expansion, and thermal conductivity are of interest (Qu et al., 2018). For example, high-temperature-tolerant insulation products, sporting goods like tennis racquets and bicycles, garments like motorcycle gloves, and other applications discussed earlier.

In this study lignin was acetylated using acetic anhydride in the presence of a catalyst. Other scientists have investigated acetylation of lignin using acetic anhydride (Jeong et al., 2012), scCO_2 (Cachet et al., 2014) and microwaves (Monteil-Rivera and Paquet, 2015). Acetylation under scCO_2 environment is a promising process as it is catalyst free and uses lower temperature. However, currently its acetic anhydride requirements are quite high. Its future depends upon the reduction of the acetic anhydride quantity utilised during the process.

The biorefinery model produces 73.55 kg/h of acetic acid, which is converted to 56.27 kg/h of acetic anhydride and consumed during acetylation. An additional 22.55 kg/h of acetic anhydride is needed to fulfil the acetylation demand. However, due to higher molecular weight of the lignin and the amount of accessible phenolic hydroxyls i.e. free hydroxyl groups, the total amount of acetic anhydride used should be much less and lower still if partial acetylation is intended. Thus, there is much scope to improve this process and considerably reduce the acetic anhydride demand. For a commercial biorefinery, this would be important to ensure economic competitiveness.

The biorefinery produces 126.31 kg/h of succinic acid which produces 51.61 kg/h of PBS all of which is consumed for the generation of CPC foam. This process generates a significant quantity of THF as a by-product. THF has application as a solvent and primarily used as a precursor for polymers such as spandex (Pruckmayr et al., 1996).

1 The biorefinery consumes 26.27 kg/h and 7.17 kg/h of CO₂ in the succinic acid production and
2 foaming processes. There is CO₂ present in the headspace of the acetic acid digester, however, it is
3 marginally consumed within the process. The presence of this CO₂ forces the *Moorella*
4 *thermoacetica* to utilise all the CO₂ that is produced during the digestion process, thereby achieving
5 higher conversion rates.

6 In the simulation DME is used in the SOFC with 50% efficiency. Published research shows the
7 promise of DME as a suitable fuel for SOFC (Murray et al., 2002; Su et al., 2011). The issue with DME
8 as a fuel for SOFC is similar to that of any other hydrocarbon fuel. It leads to coking.

9 Further breakdowns of heat and electricity demands are provided in the figures (2) and (3)
10 respectively. Pretreatment Area (A100) consumes the most heat, nearly 80% of the total demand.
11 This is due to the presence of large water content in the three main processes of fractionation, de-
12 lignification and lignin drier consuming 745.83 kW, 181 kW and 16.22 kW respectively. Research is
13 needed to develop newer processes for biomass fractionation that operate at lower temperatures
14 and/or with much less water. Carbon Fibre Area (A500) has the second highest heat duty due to the
15 carbonisation process consuming 78.53 kW of energy.

16 The large parasitic heat demand shows there is much room for improvement. This involves
17 optimisation research on energy consumption of individual processes and re-design of the overall
18 concept to incorporate alternatives with lower energy demand.

Figure 2: Hourly Heat Duty Breakdown (1165.76 kW)

Figure 3: Hourly Electricity Demand Breakdown (130.33 kWh)

Another option to consider is re-design of the biorefinery in such a manner that allows for some of the lignin to be combusted for energy generation. However, this would reduce the carbon fibre

production and detailed economic assessment would be needed for a comparison of the two models. A part of this research would entail 3- and 4-dimensional modelling of the facility for detailed investigation of the technical data.

Lastly, while the simulation results are promising and show the technical viability of a biorefinery producing biodegradable carbon fibre composite, research is still needed to optimise the reuse of the carbon fibre from the end-of-life products. One area of research is the separation of carbon fibres in usable form from the PBS matrix via biodegradation. Only then, closed materials supply chain for a circular economy (Ghayan, 2018b) can be established.

4. Conclusion

In this study a novel biorefinery model converting sawdust waste and CO₂ into carbon fibre-poly(butylene succinate) foam (CPC foam) was simulated. Results show that the biorefinery consumes 417 kg of biomass, 33 kg of CO₂, 86 kg of methanol, 23 kg of acetic anhydride, 130 kW of electricity and 1,166 kW of heat per hour. Its main products are 72 kg of CPC foam and 82 kg of carbon fibre. The facility also generates 24 kg of THF as a by-product. 50 kg of DME is produced as a side-product during the reactive distillation of acetic acid and is enough to fulfil parasitic electricity requirement of the biorefinery. A large heat demand is a major hurdle and research is needed towards its reduction. Biomass fractionation into cellulose, hemicellulose and lignin consumes the most heat, 80% of the total biorefinery demand, mainly due to the high water content in the process. There is a need to develop biomass fractionation processes that either require less water or utilise less energy intensive technologies. A continuing area of research is biological separation of the polymer from the carbon fibres and their reuse. Despite these unanswered research questions, simulation results show promise for biodegradable carbon fibre composites from lignocellulose and CO₂ playing a role in closed materials supply chain, thereby helping in the transition of linear economies to circular economies.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: