3. WP 2100 Biological nutrients report

3.1. Introduction to WP 2100 and Biological Nutrients

The purpose of this work package is to propose a concept for the use of spacecraft as biological nutrients. According to the original statement of work it shall comprise:

• Spacecraft materials particularly usable for the introduction into biological cycles.

• Description of technical concept for implementation of materials conversion process.

• Expected yield or efficiency of process, including the analysis of target products and possibly by-products as well as waste.

• Energy source(s) and estimation of energy requirements, including concepts for 'slow manufacturing'. Slow manufacturing means that the process may take several years with minimum energy requirements.

• Estimation of current TRL level and estimation of ROM costs to reach TRL 5, i.e. a breadboard validation in the (mission) relevant environment. TRL estimation is made separately for applications on earth as a reference and for a lunar mission scenario. Depending on the technology, the latter may be within a habitat or exposed to the external environment on the moon.

• Design implications with new material, considering also space environmental exposure. This assessment is relevant where mechanical or thermal requirements cannot be met, or where the space environment (radiation, vacuum), may compromise the target performance.

The work package is based on the results of TN1, TN2 and TN3. A focus in respect of the mission scenario, the nutrients of interest and other boundary conditions was suggested and agreed upon in the review of Part 1 of the project. With respect to materials, CFRP, especially CFR-PEEK, was identified as most important resource in quantitative terms. Its recycling by means of bioprocessing in order to contribute to the biomass or for other purposes was defined as primary objective. Still, there are several useful by-products of biological cycles, including O_2 from photosynthesis, CH_4 from anaerobic digestion, and H_2 from bacterial metabolism, that will favor the use of one method over another. For example, the energy requirements of phototrophic systems can be supplied simply by solar irradiance, CO_2 as well as macro- and micro-nutrients, while heterotrophic systems require biomass as a carbon source, and macro- and micro-nutrients.

As will be shown, there are several metabolic pathways to produce and degrade carbon fibers, plastics and adhesives. For both the technical and biological cycles, the best scenarios were determined. However, just as many of the manufacturing processes can be drop-in processes, many different synthesis pathways be used to produce or recycle materials, making the system extremely flexible, which was one aim of this study.

3.2. Methods for WP 2100

An intensive literature review of scientific journals, online government archives of U.S. Department of Energy, Erasmus, and NASA and Conference Proceedings and Abstracts was done to determine the State of the Art for associated bioprocessing and lunar conditions. The evaluation of the usability and feasibility of CPR-PEEK and adhesives is based on C2C criteria of recyclability, non-toxic degradation and evaluated by space agency experts.

3.3. Classification of Biological Processes by Inputs, Outputs and Energy

Resources, energy sources and outputs for the two most important bionutrient processes are summarized in Table 1. Specific processes and their outputs and energy demand are given separately in sections for CF, plastics/PEEK and adhesives.

Table 1: Overview of different metabolic strategies important to the production of precursors of CFR-PEEK (C), plastics (P), and adhesives (A)

Biological Process	Energy Sources	Inputs	Synthesis - Outputs	Organism
A. Auto-trophic				
photolitho-trophic	Light	CO_2, H_2O H_2S, H_2, nutrients	carbohydrates/sugars - P, A lipids - C, P, A , oil (fuel) enzymes - various pathways	Plants, Algae, Cyanobacteria Chlorobiaceae, Chromaticaceae
B. Hetero-trophic				
chemo-organo-hetero-trophic	Organic Oxidation	CO_2 & H from Organics (e,g, Glucose, Pyruvate)	carbohydrates/sugars - P, A lipids - C, P, A , oil (fuel) enzymes - various pathways H_2, CH_4 ethanol/lactic acids - fuels	Majority of bacteria, Fungi Methanogens Fermenters

The attributes of the value chain are illustrated in Figure 2. Inputs of inorganic chemicals and simple organic compounds generate biomass in greenhouses or bioreactors. Biomass can consist of vascular plants, alga, fungi, yeast, or bacteria or any combination of these. As cells grow and add biomass, they synthesize valuable chemicals precursors including carbohydrates (e.g. starch, sugars), aromatics (e.g. polyesters), and other hydrocarbons (e.g. lipids) [1] that can be separated in the refining process (analogous to pretreatment in the technical cycle). The resulting value chain for the synthesis of biomaterial shows how these raw material are converted to bioproducts such as plastics, adhesives, composites via different methods including, fermentation, hydrolysis, combustion and subsequently used in the technical cycle to manufacture components.
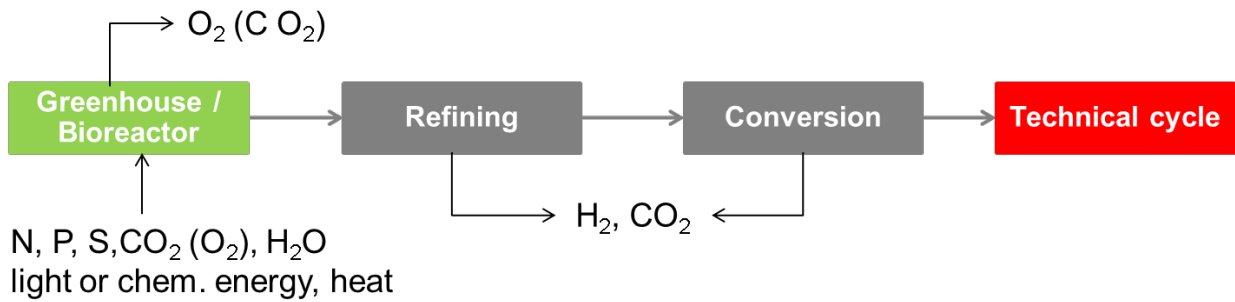
Figure 2: Generic biological value chain

Figure 3 depicts the generic process to produce CF, PEEK/Plastics and adhesives along the value chain. This example applies to algae, yeast, bacteria, and fungi either alone or synergistically.
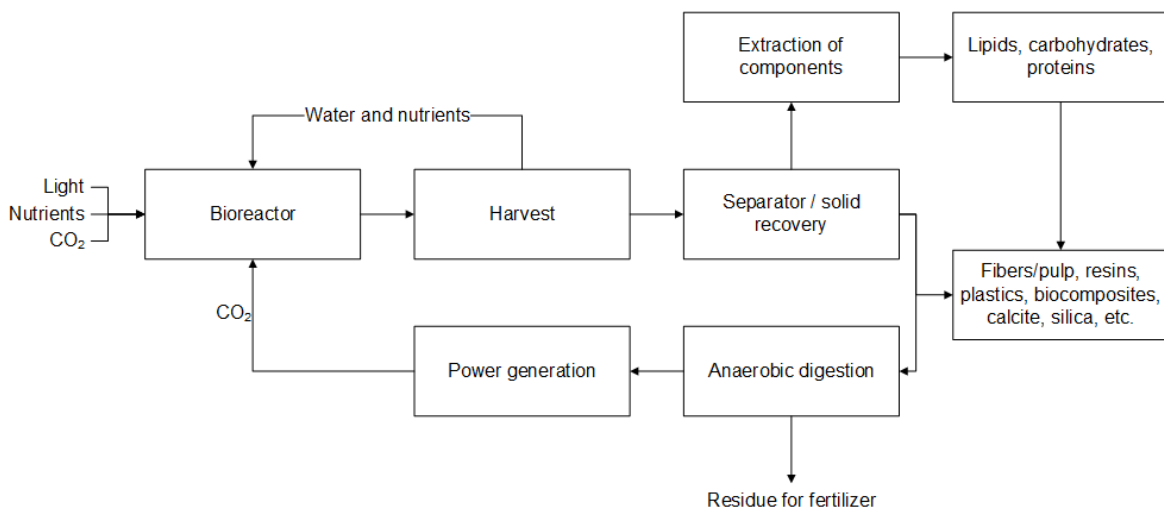

Figure 3: Generic process to produce CF, PEEK/Plastics and adhesives along the value chain

3.4.   General concept and evaluation aspects

Figure 4 shows cycles for biological and technical nutrients for this SMC project on the moon. The periodic supply of material from the spacecraft will enter the cycles via recycling and AM processing. Virgin CFR-PEEK will be produced via biological synthesis. Other end products can be generated depending on the microbial organisms of the bioreactors and the related nutrients supplied.

The production of CFR-PEEK is achieved by coating carbon fibers (CF) in a PEEK plastic resin to thereby providing CF reinforcing (CFR). Both CF and PEEK can be produced from microbial synthesis via polymer precursors. Although many of the same bio-polymers can be used as precursors for both CF and PEEK production (as well as other plastics and adhesives), here they are treated separately as Plastics/PEEK, CF and adhesive processes in sections 3.5, 3.6 and 3.7, respectively, in order to more clearly illustrate each process. These same CFR-PEEK materials can be recycled, to some extent and biodegraded, which will also be discussed

separately in each section. Overall, the concept is the integration of biomaterials into the technical cycle for additive manufacturing, completing the C2C approach. Interestingly, NASA has placed more value on additive manufacturing using biomaterials from silk (e.g. spider and silkworm) bioengineered from bacteria than on CFR [2]. However, the approach we present here was not part of their analysis.
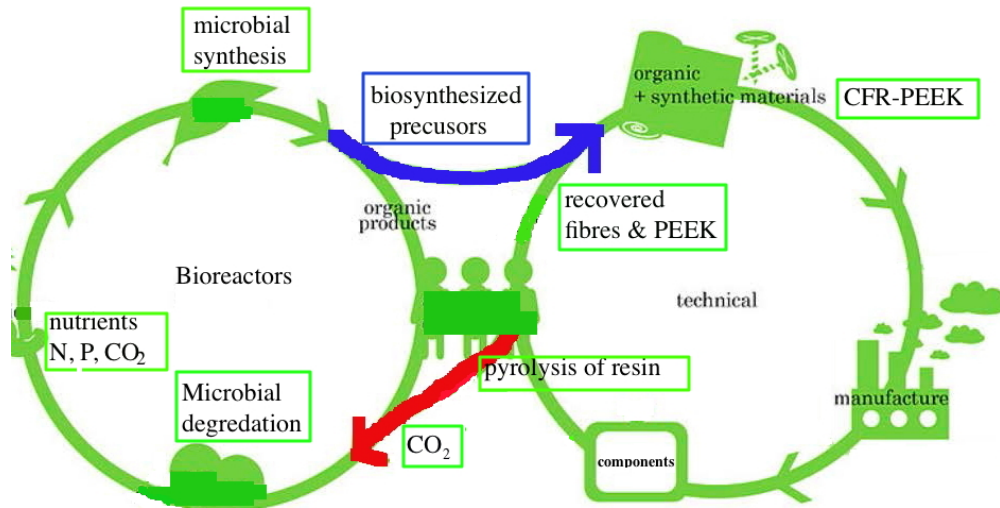

Figure 4: C2C approach for this study

3.5. Outcome: Plastics

3.5.1. Scenario framework

Polyether ether ketone (PEEK) is a colourless thermoplastic, crystalline (30-35%) polymer that is typically synthesized from aromatic dichlorides in a polar aprotic solvent (Figure 5).
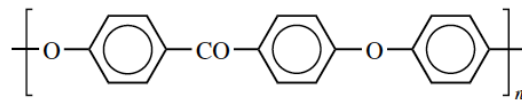

Figure 5: PEEK polymer

Specifically, PEEK polymers are produced from bisphenolates (e.g. 4,4,-difluorobenzophenone) reacted with salts of hydroquinone. There are a variety of biological pathways for polymers that could be precursors for hydroquinone and bisphenolate. PEEK can be used continuously to 250°C and in hot water or steam without permanent loss in physical properties. In hostile environments, PEEK offers a high strength alternative to fluoropolymers.

3.5.2. Recycling value chain design

Carbon fibers reinforced with a PEEK resin are a good structural reinforcement for bearing applications. Still, the introduction of reinforcement PEEK makes the recycling process more difficult. Some treatment processed for degrading PEEK may not remove contaminants or

restore the polymer. Recycling CFR-PEEK, not only recovers materials, mostly fibers, but also provides an energetic savings compared to metals (Table 2). The environmental advantages of recycling Peek are that it does not leach toxic substances that can effect cell metabolism [3] and has a V-O flammability rating, producing very less smoke and toxic gas emissions when exposed to flame. When overheated or combusted PEEK, will produce carbon monoxide and carbon dioxide, however, these could be used for in the biological nutrient cycle by photosynthetic algae or anaerobic processes.

Table 2: Energy intensity for the production of fibers and resins [4]

Material	Type	Energy intensity (MJ/kg)
Resins	Polyester	63-78
	Epoxy	76-80
	PP	72-112
Fibers	CF	182-286
Metals	Aluminum	196-257

PEEK melts at 343°C and is resistant to chemical and radiological dosing, which is why it is used in the aerospace sector. PEEK does not decompose at its melting temperature but may lose some physical properties past the melting point [5]. However, it can be recycled in the melt phase. But, like many plastics, PEEK recyclability depends more on the component design than on the chemical nature. While PEEK is not being recycled extensively at the present, the increased use of PEEK has prompted new research on how to recover it. Generally, the methods used to manage PEEK waste streams are listed in Table 3.

Based on the C2C approach and the current level of technology, the last 3 methods for plastic/PEEK recycling are recommended to recover polymers while preserving fibers. Of these three processes, solvolysis is already done at the commercial scale (e.g. CreaSolv®), while co-solvent and biodegradation processes still need to be scaled-up and tested under realistic environmental conditions [6]. The main products of the thermal decomposition and solvolysis recycling of PEEK are CO_2, CO, (by products that can be used in photobioreactors) and precursors polymers (e.g. BPA, 4-Phenoxyphenol and 1,4-diphenoxybenzene), which can be returned to the PEEK production process.

Solvolysis has been modified to recover resin precursors without toxic effects using either water and safe solvents, so called GRAS. Further, GRAS solvents can improve the solubility of the reaction products such that fibers are less contaminated by resin residue when recovered. The process recovers phenol derivatives without stirring or cooling, which are detrimental to recovery and fiber separation (Table 4). PEEK is also soluble in concentrated sulfuric acid at 25°C and could be recycled by purifying an acidic PEEK solution.

Table 3: PEEK waste management methods

Process	Pros	Cons	Costs	Earth[1] TRL	Lunar[1] TRL
Incineration	volume reduction	no material recovery, residues, off gassing	+++	8	1
Thermolysis	decomposed polymers	weakened PEEK	+++	8	1
Mechanical	simple processing	only short fibers	+	8	1
Solvolysis	fiber, monomer recovery	uses solvents	+++	8	1
Co-solvent	fibers, precursors	high temperature	+++++	4	1
Biodegradation	recovers precursors BPA	variable recovery rates	+++	3	1
1. Current technology on earth; Lunar technology from ESA technology development route.					

Table 4: GRAS solvent substitutes used in Solvolysis

Gras	%vol	°C	bar	% recovered (30 min for 39 g/L)
2-propanol	0.2	350	83	72
Acetone	0.8	350	235	93
CO_2	300	81	39 model resin	
CO_2	300	81	65 composite	
H_2O	1	350	155	84 (60 min & 10 g/L)

Co-solvent recovery is a new method that uses a 20% ethanol: 80% water (v/v) mixture at 350°C and 17 MPa for <30 min to recover fibers [7]. Supercritical fluid swells polymers to more macro-porous structures for easy separation [8]). When used with specific catalysts, monomers can be recovered, giving clean carbon fibers without washing, although some residual catalyst (cesium carbonate, 10 g/L) may remain [7]. The main by-products of the thermal oxidative decomposition of PEEK are CO_2, CO, 4-Phenoxyphenol and 1,4-diphenoxybenzene, polymers, which could be used for PEEK production or biodegraded in a high pressure bomb reactor to carryout the polymer degradation reactions. While fiber recovery is good (>80%), fibers are weakened and shorten and resins are lost [6].

PEEK precursors can also be recovered when PEEK is decomposed biologically. The cyanobacteria *Anabaena flos-aquae* has achieved high biodegradation of polyesters via transesterification of side chains via two pathways [9]

1) C16 → C14 → C12 → C10 → C8, and
2) C16 → C15→ C13 → C11 → C9

The aerobic bacterium *Pseudomonas testosteroni uses a* novel pathway involving oxidative skeletal rearrangement to metabolize BPA [10]. Renewable plastics that can be biodegraded by microbes are PHAs (polyhydroxy alkanoates [11], PLGAs (poly(lactic-co-glycolic acid), PGAs, poly(glycolic acid) and PLAs poly(lactic acid) [12]. As with CFRs, mixtures of fungi and bacteria decompose and ferment terpene crystalline diol with 70% recovery rates for a maximum of 48 hours [13]. Choi and Lee [14] developed *Escherichia coli* strains that are capable of producing short-chain alkanes (SCAs; petrol), and free fatty acids, esters and alcohols through the fatty acyl to fatty acid to fatty acyl-CoA pathway.

3.5.3. Technical aspects: Material

Several biosynthesis pathways are promising for the production of plastic polymers. Biosynthesis is also important since the transformation of benzenes to derivatives is a chemically difficult process that has poor yields and mixed products that contaminate the plastics in chemical synthesis of these polymers, including the electrophilic aromatic substitution of acyl and sulfonyl halides on aromatic reactants and the nickel catalyzed aromatic coupling of aromatic dihalides [15, 16].

Biological synthesis is a growing field that has many successes for producing polymers for plastics. For example, biotransformation of fluorobenze with *Pseudanomas mendocina*-KR1 has resulted in a high yield of a diphenol as a function of the ratio of the biocatalyst to substrate [17]. *Escherichia coli* strains have produced short-chain alkanes (SCAs; petrol), free fatty acids (FFAs), fatty esters and fatty alcohols via the metobolic pathway from fatty acyl to fatty acid to fatty acyl-CoA produced 2,3-Butanediol by microbial fermentation of carbohydrate feedstock [18].

Virgin PEEK is needed to replace PEEK polymers lost during the recycling process. Bisphenolate compounds, such as 4'-difluorobenzophenone, as well as disodium hydroquinone, can be biologically produced. Selective productions bisphenol A (BPA) polymers from mixed BPA isomers were tested in 330 strains of cells and 2 strains could produced optically pure BPA [19]. Peek can also be synthesized using 2,3-butanediol with phthaloyl chloride [20] and anaerobic microbial fermentation can also produce butanediol.

Disodium hydroquinone can be produced by microbial synthesis of quinic acid (70 g/L) from D-glucose. The acid is transformed into hydroquinone using sodium hypochlorite, bleach with 87% yield. The bacteria *Klebsiella pneumoniae* has a wide range of substrate specificity range to transform dihydroxylated compounds into quinones [21].

3.5.3.1. PEEK production from bio-polymers

The steps for PEEK production are:

1) In a three-necked flask fitted with a Dean-Stark trap, condenser, nitrogen inlet, and mechanical, 4,4' - difluorobenzophenone is mixed with hydroquinone and anhydrous potassium carbonate in a gram ratio of 1 to 0.49 to 0.95.
2) Toluene (26 ml/g) is added to remove water.
3) To initiate polymerization, the flask placed in a microwave, set to 700W and 2455 MHz, and kept from 80-110°C under reflux for 20 minutes with constant stirring.
4) The water generated during the formation of the phenate is removed by azeotropic distillation (where the addition of solvent, reduced the boiling point) or membrane sieve.
5) Toluene is removed by distillation at 110-130°C for 15 minutes.
6) For final polymerization the temperature is elevated to 180- 200°C (time varies, but < 24h).
7) The reaction is cooled to 25°C and the polymer precipitated in water.
8) Polymer is refluxed with water in Soxhlet distllation system using methanol.
9) The polymer is cleaned to remove inorganic salts and dried under vacuum 0.12 bar at 100°C for 24h.

New sources of PEEK, other plastics, and adhesives exist from various chemical synthesis pathways [3] and many improved methods are being developed for bio-polymer production,

Therefore, it seems likely that biologically produced PEEK, and plastics and adhesives in general, will achieve a commercial scale in near future.

3.5.4.   Technical aspects: Equipment

PEEK Production requires a Dean-Stark trap, flasks, distillation and condenser systems, N_2, tubing, pumps, and a 700 W microwave and a vacuum dryer. An industrial fermenter will produce hydroquinone (Figure 6).

Figure 6: Dean-Stark trap (from left to right) with distillation and condenser system, vacuum dryer, a fermenter reactor and a Soxhlet still

PEEK Recycling
- Solvolysis requires a batch reactor (which can optionally be made of recycled material).
- Co-solvent process requires a metal pressure vessel (Figure 7).
- Biodegradation requires a bioreactor.

Figure 7: Reactors for PEEK cycling for resin recovery

All process systems require small motors/pumps and connectors/tubing. All processes can be made continuous flow-through using sensors and a controller. Various components and can be

made of recycled material. For production processes, PEEK reactors are preferred and can be produced/recycled.

The interfaces relevant for bioreactor recycling and production are assessed against the assumptions pre-defined by the scope of this project. The final selection of relevant interfaces shall serve as set of criteria to evaluate the applicability of biochemical technologies on the moon, as defined by the mission scenario. Upgrading of these processes is summarized in Table 5.

Table 5: Upgrading for recommended PEEK production and recycling

PEEK Production	Current TRL	TRL 5 Upgrade[1] Costs (Mio€)	Output[2] kg/y/reactor	Energy Used[3] MJ/y
BPA polymers	3	<0.5	4110	10^5
2,3-butanediol fermentation	3	<0.5	315	10^5
diphenol	3	<0.5	42	10^5
quinic acid algae bacteria	3	<0.5	50	10^5
Recycling				
Solvolysis	8	0	10^3	$2x10^4$
GRAS solvents	4	<0.5	10^4	$2x10^4$
Co-solvent	4	<0.5	$5x10^2$	10^5
Biodegradation	3	<1	10^4	10^5
1. Cost estimation to reach TRL5 based on cost estimation according to the following pattern: - Single engineering project and validation: <0.5 Mio€ <1 Mio€ <2 Mio€ - Joint engineering and research project of 2-3 partners: <2 Mio€ <5 Mio€ <10 Mio€				
2. Assumes a 200 l bioreactor volume.				
3. Biological reactors based on commercial systems made of PEEK and operated with electricity for stirring and heating.				

Like the environmental conditions for the moon factory, there are specific conditions necessary for reactors to optimally operate for recycling and production in the bionutrient cycle.

1. **Atmosphere**: The atmosphere interface, which may expose reactors to dust and trace gases, is not so important since reactors will operated as closed systems. However, the lack of O_2 may be beneficial for anaerobic processes and pyrolysis.

2. **Radiation:** Shielding from cosmic and climate control will be required to protect organisms in bioreactors. Radiation levels for microbial organisms should be maintained at or below 488 ᶊ Sv/d. However, visible light (400 nm-700 nm) should be transmitted for active photosynthesis in bioreactors. Since the moon has up to 100°C in the daytime and -173°C at night, a heating/cooling system would also be required to maintain bioreactors at their optimum temperature, which is process dependent. However, it may be possible to take advantage of extreme heating to augment biochemical reactions and cool processes.

3. **Energy:** Electric energy will be required to operate components of the bioreactors and processing equipment, however the power demand will be low. It is assumed that energy supply is ensured but limited. Thus, the interface **is not considered as relevant**

interface on the moon. It is important to note the biological production and recycling processes are dependent on biochemical reactions, which liberate internal energy and drive the synthesis of the biomaterials. The low energy demand of reactors and equipment for recycling and production of CPR-PEEK   could be provided solely with photovoltaic modules.

4. **Force:** One of the largest unknowns is the effect of microgravity on reactor functions, especially microbial growth, synthesis and metabolism in bioreactors. However, on going work in our laboratory will elucidate this under different culture conditions.

5. **Material:** Since the project excludes the use of material available on the moon, the only source of materials is recycled components from the spacecraft. However, since recycling cannot provide 100% material recovery, virgin biomaterials can be produced via synthesis in bioreactors. The use of PEEK bioreactors will also allow continuous production of reactors on the moon. Metal components for reactors systems, could be made from recycled aluminum.

6. **Medium:** The use of regolith that could be processed to a medium (e.g. O_2) is not part of this project, no is life support systems. Media is extremely important to bioreactor operations, particularly CO_2 for photosynthesis, O_2 for aerobic metabolism and thermal processes, and nutrients for microbial growth. Concentrated nutrients could be transported by spacecraft and used as needed for biosynthesis. CO_2 could be generated by pyrolysis of contaminated materials and used to drive photosynthetic processes in bioreactors. The by-product of photosynthesis is O_2, which could be recovered for aerobic bioreactors and thermal processes.

7. **Space**: Spacing is **considered irrelevant** for the production and recycling technologies since they have a small spatial footprint.

A summary of the interfaces considered important for biological production and recycling processes (radiation, force and materials, and medium) are given in Table 6.

Table 6: Characterization and evaluation CFR-PEEK processes

Interface	Positive and Negative interactions	Suggested Solution	Suitability
Radiation	- Shielding cosmic and UV radiation	Plastic structure	+++
	+ Transmission of visible light	Semi-transparent PV panels	++++
	-/+ Cooling and heating augmented	outer pumps	+++
Force	- Fluid flow independency on gravity	Experiments needed	
	-/+ Microbial growth independency on gravity	Experiments needed	
Material	+ Low effort to sort material	Current technologies	++++
	+ Recycled space ship materials	Current technologies	++++
	+ Virgin biomaterial production added	New bioreactor design	++++
	- Contamination of recycled material	EOL-Pyrolysis	++++
Medium	+Low number of different media	Bio-production	+++
	-Limited media supply	Recycling	+++

3.5.5.   Feasibility evaluation

Feasibility of plastic/PEEK production and recycling is based on the entire life cycle for the process, and is assessed for current levels of technology, prospects for future technologies, complexity and required effort. Expert were asked to assess the feasibility and suitability of different processes and their answers were factored into the evaluation in Table 7. Based on the evaluation, a preferred option was selected.

State of the art

The production of BPA is currently commercially produced (1 ton/y). Commercial production of 2,3-butanediol from biological processes is in its early stages, however, future research into more efficient processes and technologies can be expected to increase. Because bioreactors need to be matched to an organism or biosynthesis pathway, specific bioreactors will be needed to produce specific polymers. This too is a growing area of research. The use of fermenters in industry is one example, and the use of photo-bioreactors for algal production is another.

Table 7: Feasibility of PEEK production and recycling

PEEK Production	Experts[1] surveyed	Lunar[2] TRL	Current[2] TRL	Future[2] TRL	Comple-xity	Effort	Total Score
BPA polymers							
2,3-butanediol fermentation	4	1	4	5	2	3	17
diphenol quinic acid							
algae	4	1	4	5	4	4	22
bacteria	2	1	4	5	2	3	17
Recycling							
Solvolysis	3	1	5	5	2	3	19
Co-solvent	2	1	2	2	3	2	12
Biodegradation	1	1	1	3	2	2	10
1. Answers from 4 of 12 experts in either a written or telephone survey, added to our opinions. 2. Scores range from 1 = unfavorable to 5 = favorable. Total score maximum is 30 points.							

Conceptual layout of preferred option

Based on the above evaluation, the following processes were preferred for the sustainable materials concept at the lunar South Pole.

- bioreactors coupled to with Solvolysis to recover monomers of PEEK.

- bioreactors to produce bisphenolates for PEEK.

- Pyrolysis of EOL PEEK to produce CO_2 for photo-bioreactors (i.e. 890g CO_2/kg Peek, [22]).

3.6. Outcome: Carbon fibers

About 90% of the carbon fibers are made from polyacrylonitrile (PAN) with the remainder from rayon or petroleum pitch [23]. PAN is an organic polymer, characterized by long strings of molecules bound together by carbon atoms. Biological sources of PAN could be synthesized from simple feedstock such as cellulosic sugars and lipids to produce the acrylonitrile precursor.

The CF production steps are:

1) PAN is polymerized by adding acrylonitrile with methyl acrylate and a catalyst in solution.

2) To produce fibers, PAN is carbonized at 1000-3000°C without O_2 to produce long strands and expel non-carbon atoms, leaving a long, tight chains of carbon atoms.

3) Fibers are washed and stretched to desired size.

4) Fibers are heated from 200-300°C in air (or O_2) for 30-120 minutes so O_2 is bonded, fibers rearranged both of which modify the surface of the fiber to more easily bond with resins.

5) Finally resins are added to coat the fibers and wound into yarns of various sizes.

3.6.1. Recycling value chain design

Carbon fibers are usually extracted from used components by breaking down resins in pyrolytic or chemical processes (Figure 8). Biodegradation is a new field that shows promise. These processes are summarized in Table 8.
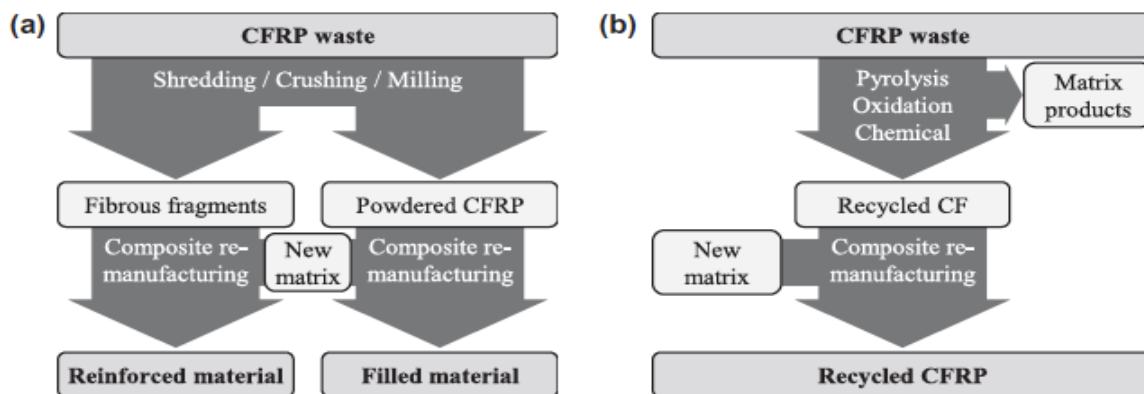

Figure 8: Mechanical, thermal and chemical CF recovery processes [24]

Table 8: CRF recycling, based on [24]

Process	Pros	Cons	Costs	Earth[1] TRL	Lunar[1] TRL
Mechanical	no toxins produced	> 50% fiber degradation	+	8	1
Chemical	retains properties	solvents, low contamination tolerance	+++	8	1
Fluidized-bed	clean fibers	25-50% fiber loss	++++	3	2
Pyrolysis	retains fiber property resin precursors	solvents, CO, CO_2 off gassing	+++	8	1
Solvolysis	composite recover < 20% fiber loss	uses solvents	+++	8	1
Co-solvent	fibers, precursors	high temperature	+++++	4	1
Biodegradation	fibers, precursors	variable recovery rates	+++	3	1
1. Current technology on earth; Lunar technology from ESA technology development route.					

Similar to PEEK recycling, the last 3 recycling methods are recommended for CFR recycling because they preserve both fibers and polymers. In contrast to PEEK recycling, they are conditions when pyrolysis should also be used, for example when the fibers are contaminated, too short for recovery and at the end of life (EOL). Of these four processes only pyrolysis and solvolysis are available commercially (Table 9). As discussed for PEEK, co-solvent and biodegradation processes still need to be scaled-up and tested under realistic conditions.

Table 9: Commercial CF recycling companies

Company	Location	Process	Output	Comments
MIT-RCF	USA	Modified pyrolysis	fibers	
AFRA Assoc.*	USA	Pyrolysis	fibers	
ELG Carbon Fibre Ltd	UK	Pyrolysis	fibers	
Formoso Tech.	ES	Pyrolysis	fiber	Pilot Plant
Karborek Spa	IT	Pyrolysis, O_2	fibers	
Alenia Aeronautica	IT	Pyrolysis		
CFK Valley Recycling	DE	Pyrolysis	fibers	
Hadeg Recycling	DE	Pyrolysis	fibers	
Toray Indust. Inc.	JA	Pyrolysis	fibers	
Siemens	DE	Solvolysis	monomers, fibers	
Adherent Technol Inc.	USA	Wet Chemical	99% fiber	
Unknown (Temas AG)	CH	Microbial	fibers, alcohols	Trade Secret
SGL Group	DE	Trade Secret	fibers	Trade Secret
*27 firms in association				

Given an optimal thermal system and biodegradability of the material, pyrolysis produces gas (6 MJ/kg) oil (20 MJ/kg) and char (20 MJ/kg) as well as fiber recovery. It can be separated into slow processes, which require temperatures from 400-900°C for long time periods, and rapid processes, which require rapid heating (>1000°C) followed by cooling to 650°C. Rapid processing produces more oil from biodegradable materials and less char, than slow processing,

but is more energy intensive. However, the output–input energy ratio 13.2, indicating the high energy and the total net carbon emission is 176.6 kg CO_2/m^3 of oil.

Both Adherent Inc. [25] and Siemens Corporate Technology, have technologies to recycle fibers and resin precursors, where composites are heated under pressure at low temperatures (e.g. 200°C) and converted to low molecular-weight soluble alcohols with the help of water. No environmentally damaging solvents are used in the process, which also requires much less energy than would be required to manufacture new fibers. The fibers remain intact and mechanical properties are nearly fully retained so fiber can be directly processed.

Several microbial processes also exist to decompose CFR to alcohols and fibers (e.g. TEMAS AG), but these are not yet scaled to the commercial level. Biodegradation has been demonstrated on various nano-carbon products, which when exposed to microbes, will growth a biofilm on surfaces [26]. This is because fiber surfaces and resins supply enough carbon for microbial growth, so that CFR are not immune to adhesion of environmental microflora, and attack of materials [26, 27].

During biodegradation polymer too big to enter cells are first converted to its monomers [28]. The initial breakdown of a polymer can result from a variety of physical forces, such as heating/cooling, freezing/thawing, or wetting/drying, that cause mechanical damage such as the cracking of polymeric materials. Nakamura et al. [29] noted photodegradation of PEEK caused embrittled sheets. Abiotic hydrolysis is the most important reaction for initiating the environmental degradation of polymer solids. Fungal growth penetrates bio-polymers and synthetic polymer solids causing small-scale swelling and bursting. Biodegradation of previously non-biodegradable polyesters can also be improved with thermophilic hydrolase at 65°C, which may be applicable to synthetic polymers that have not previously been at all degradable.

Complete polyester biodegradation has been demonstrated by microbial synergy [30, 31]. For example actinomycetes (fungi) depolymerize polyesters (but cannot metabolize products), while other bacteria secrete extracellular depolymerases and hydrolytic enzymes to enhance cleavage and facilitate uptake into metabolic pathways [28]. Bacteria attached to cellulose nanofibrils on surfaces fibers mediate substrate during the fermentation process of bacterial cellulose [32]. The adhesion between the deposited cellulose and the fibers is enhanced by a solvent extraction to remove hydrophobic compounds from the fiber surface.

New carbon fiber composites could be made more sustainable by using or partially renewable biopolymers as resins [33]. Cellulose acetate butyrate (CAB), polylactic acid (PLA) or Sorona (Dupont) are all natural fibers that are low cost, low density, high abundance, and are biodegradable, and so renewable.

3.6.2. Technical aspects: Material

PAN Precursors

Production of acrylonitrile for PAN is illustrated below with ammonization of propylene in the Sohio process,

$2CH_3-CH=CH_2 + 2NH_3 + 3O_2 \rightarrow 2CH_2=CH-C\equiv N + 6H_2O$
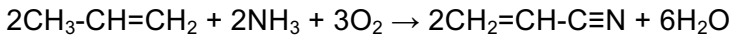
Propylene (propene), ammonia (g) and air are heated to 400–510°C and 0.5-2 bar, then quenched in aqueous sulfuric acid to produce an aqueous solution, as well as acetonitrile, hydrocyanic acid, and ammonium sulfate. Acrylonitrile and acetonitrile are separated by distillation and water removed by the recovery column.

A production route for green propene (green arrows) and 1,3-butadiene at the pilot plant scale is shown in Figure 9 starting from triglyceride and fatty acid based biomass [34], which can be produced by bacteria [35] (yellow arrows) and algae [36] (green arrows). Further, many different bioproducts from algae and bacteria could also be produced following different pathways [37] (black arrows)
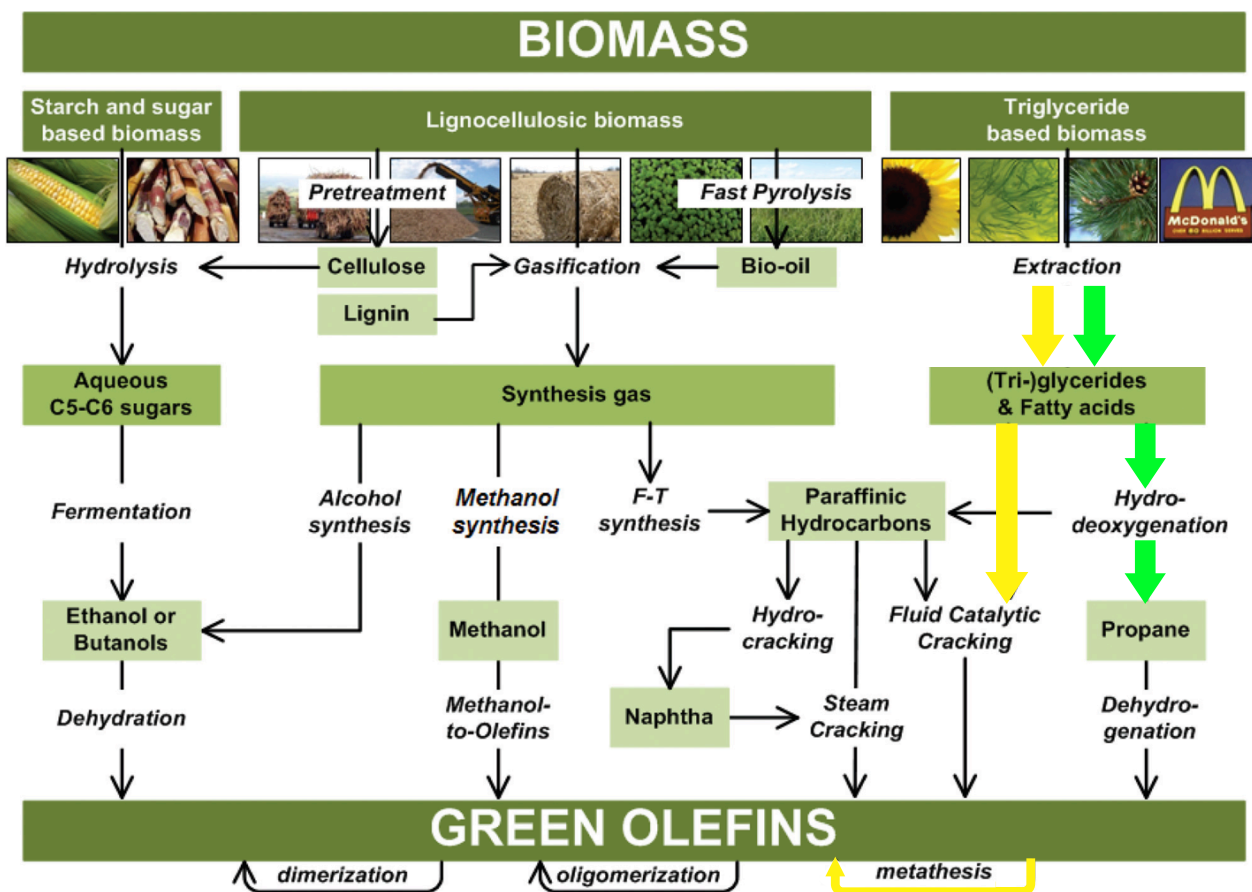

Figure 9: Biological production of PAN-precursors (from [34]). The arrows indicate mass flows where the green (algae) and yellow (bacteria) arrows show the preferred bionutrients processes.

Propene is also a product of glycerol hydro-deoxygenate produced from microbial fermentation and metabolism [38]. Under the standard [39] reaction conditions (300°C temperature, 8.0 MPa hydrogen pressure), glycerol conversion exceeds 88% and selectivity to propene reaches 76% after 6 hours of reaction. While biomass in Figure 9 could be used to produce PAN for carbon fibers, it could also be used to produce other plastics. Bio-based PET, recycled PET, and recycled (partially) bio-based PET, PLA (polylactic acid, a bio-based polyester) and man-made

cellulose fibers all have low environmental impacts [39, 40]. In the future, polyester polyols with different structure and different molecular weight from dicarboxylic acids and diols could be used in the production of polyurethanes that are biodegradable and biocompostable [41]. Therefore, it can be seen that the sustainability of bioplastics is high when they are produced from renewable oils and refinery bio-wastes, which render synthetic polymers renewable without impairing their property profiles and recycling [42].

A recent U.S. Department of Energy report found that the source type, quantity of chemical impurities, and the degree of pre-polymerization are three critical factors that need to be addressed of bio-PAN polymers [43]. Shlyahtin et al. [44] have revised the acrylonitrile copolymer process using CO_2 and without solvents or surfactants, thereby making it a sustainable, green process (Figure 10).
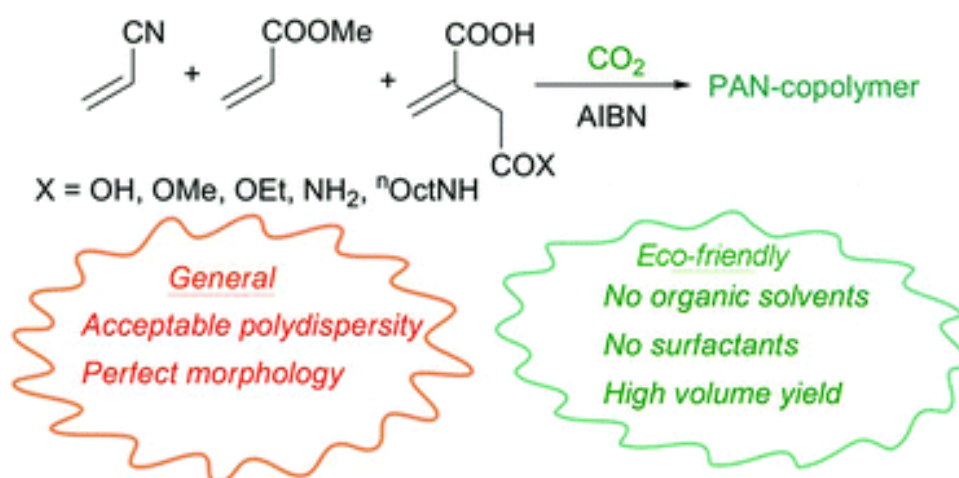

Figure 10: Green PAN-precursor process

Algae and bacteria are prime sources of sugars and many algae are rich in oils, which could serve as precursors for bio-Pan. These organisms are routinely grown in specially designed and operated bioreactors to synthesize such polymers.

3.6.3. Technical aspects: Equipment

CF production requires a photobioreactor, Soxhlet still, reactor connected to a furnace, both with O_2, batch reactor as a wash, a centrifuge, distillation column and machinery for fiber stretching and sizing (Figure 11).

Figure 11: Photo-bioreactor (top left), furnace (top right),
centrifuge (bottom left) and stretching machinery (bottom right).

CF Recycling
- Pyrolysis requires a furnace without O_2.
- Solvolysis requires a batch reactor, which can be made of recycled material.
- Co-solvent process requires a metal pressure vessel, which can be recycled metal.
- Biodegradation requires a bioreactor, which can be made of recycled materials.

All process systems require small motors/pumps and connectors/tubing. All processes can be made continuous flow-through using sensors and a controller. Reactor components and flasks/traps can be made of recycled material. High pressure vessels and high temperature vessels can be made of recycled metal. For production processes, PEEK reactors are preferred and can be produced/recycled.

The interfaces relevant for bioreactor recycling and production are assessed against the assumptions pre-defined by the scope of the SMC project. The final selection of relevant interfaces shall serve as set of criteria to evaluate the applicability of biochemical technologies on the moon, as defined by the mission scenario.

Like the environmental conditions for the moon factory, there are specific conditions necessary for reactors to optimally operate for recycling and production in the bionutrient cycle.

These interfaces are identical to those in section 3.5.4.

Table 10: Upgrading for recommended CF production and recycling

CF Production	Current TRL	TRL 5 Upgrade[1] Costs (Mio€)	Output[2] kg/y/reactor	Energy Used[3] MJ/y
propene/ethene/butadiene from				
algae	4	<0.5	10^3	10^5
bacteria	4	<0.5	10^3	10^5
dicarboxylic acids	3	<1	ND[4]	10^5
diols	3	<1	ND[4]	10^5
Recycling				
Pyrolysis	8	0	10^4	4×10^5
GRAS	4	<1	10^4	4×10^5
GRAS solvents	4	<1	10^3	2×10^4
Co-solvent	4	<1	5×10^2	10^5
Biodegradation	3	<2	10^4	10^5
1. Cost estimation to reach TRL5 based on cost estimation according to the following pattern: - Single engineering project and validation: <0.5 Mio€ <1 Mio€ <2 Mio€ - Joint engineering and research project of 2-3 partners: <2 Mio€ <5 Mio€ <10 Mio€				
2. Assumes a 200 l bioreactor volume.				
3. Biological reactors based on commercial systems made of PEEK and operated with electricity for stirring and heating.				
4. ND indicates no data available for this process.				

3.6.4. Feasibility evaluation

3.6.4.1. General

Feasibility of CF production and recycling is based on the entire life cycle for the C2C process, and is assessed for current levels of technology, prospects for future technologies, complexity and required effort. Experts were asked to assess the feasibility and suitability of different processes and their answers were factored into the evaluation in Tables 7 and 11. Based on the evaluation, a preferred option was selected.

3.6.4.2. State of the art and conceptual layout of preferred option

Polymers from photo-bioreactors no experiments can produce the polymers needed for CF production, although there are no commercial facilities currently in operation. The gap in knowledge is that space experiments with algal bioreactors for CO_2 uptake and O_2 generation have only been proposed as part of life support system, for instance algal photo-bioreactors on ISS [45]. It is known that care must be take to protect photosynthetic cells from harmful radiation while at the same time exposing them optimal levels of visible solar irradiance [46], therefore new designs are needed to accomplish this. The same applies to fermenters and heterotrophic bioreactors since they too need to be protected from cosmic and ultraviolet radiation [47]. While all of these proposed processes work individually, the challenge will be to integrate them such that virgin materials can be generated to supplement recycled materials, with feedbacks and controls and utilization of by products, e.g. O_2 from photo-bioreactors and CO_2 from fermenters and pyrolysis.

Table 11: Feasibility of CF production and recycling

CF Production	Experts[1] surveyed	Lunar[2] TRL	Current[2] TRL	Future[2] TRL	Comple-xity	Effort	Total Score
propene/ethene /butadiene from							
algae	4	1	3	5	2	2	17
bacteria	3	1	4	5	2	3	18
dicarboxylic acids & diols, microbial	3	1	4	4	2	3	15
Recycling							
Pyrolysis	4	1	5	5	3	3	21
Solvolysis	4	1	5	5	2	3	20
Co-solvent	2	1	2	2	3	2	12
Biodegradation	1	1	1	3	2	2	10
1. Answers from 4 of 12 experts in either a written or telephone survey, added to our opinions. 2. Scores range from 1 = unfavorable to 5 = favorable. Total score maximum is 30 points.							

Based on the evaluation in section 3.6.4, the following processes were preferred for the sustainable materials concept at the lunar South Pole.
- bioreactors coupled to Solvolysis for CF and resin recovery
- bioreactors to produce propylene (CF precursor) and processing CF.

3.7. Outcome: Adhesives

3.7.1. Scenario framework

Many permanent, biodegradable adhesives are formed from covalent cross-linking and are either chemically synthesized [48] or from biological sources, such as macroalgae [49, 50], microorganisms [51], and invertebrates [52]. Bacteria and algae utilize polysaccarides and carbohydrate exopolymers to achieve bond strengths up to 500 000 N/m^2 [53] while macroalgae also use polyphenolic proteins containing L-DOPA, a hydroxylated amino acid, tyrosine [54].

An increasing number of manufacturing processes are using various forms of glues and adhesives to replace stitching, stapling, and less effective fastening methods. Adhesives based on plant oils, fatty acids [55], edible sugars [56], plant proteins, and phenol resin [57] have all been subjects of recent studies. The commercialization of carbohydrates by extraction [58] and biocatalysts [59] is new and expanding field of study, not only for adhesives but for the food industry [60].

3.7.2. Recycling value chain design

Table 12 summarizes the recycling processes for adhesives. Mechanical recycling consists of separating and grinding adhesives to a powder. Fluidized beds and pyrolysis do not recover precursors, but can be used for EOL processing. As with plastics, chemical processes require solvents, although solvolysis with GRAS can recover adhesive precursors without toxic effects.

Table 12: Adhesives Recycling

Process	Pros	Cons	Costs	Earth[1] TRL	Lunar[1] TRL
Mechanical	simple, no toxins produced		+	8	1
Fluidized-bed			++++	3	1
Pyrolysis		no recovery	+++		**1**
Chemical	toxins	solvents	+++	8	1
Solvolysis	no toxins		+++	8	1
Biodegradation	no toxins		+++	3	1
1. Current technology on earth; Lunar technology from ESA technology development route.					

3.7.3. Technical aspects: Material

The most promising adhesive are pressure sensitive adhesives produced from plant oils [55]. Several chemical companies in the USA are interested in developing a high volume product. Most commercially bio adhesives are used for medical applications. Currently, only Synaero (HemCon Medical Technologies Inc.) and Nu-Knit and Surgical (both Johnson and Johnson) are produced from plant polysaccarides are commercially available. Two acrylated resins based on soybean oil have been scaled up and oleic acid methyl ester (from vegetable oil) has been scaled up.

3.7.4. Technical aspects: Equipment

The production and recycling of bioadhesives will use similar biotechnology as the mentioned in sections 3.5.4 and 3.6.3. Therefore, the environmental conditions for producing and recycling bioadhesives in a moon factory, will be identical to those in section 3.5.4. Upgrading based on specific adhesive production and recycling components is summarized in Table 13.

Table 13: Upgrading for recommended adhesive production and recycling

Adhesive Production	Current TRL	TRL 5 Upgrade[1]	Output[2]	Energy Used[3]
		Costs (Mio€)	kg/Y/reactor	MJ/y
lipids/FA				
algae	3	<1	10^3	10^5
bacteria	3	<1	10^3	10^5
polysaccarides				
algae	3	<1	10^3	10^5
bacteria	4	<1	10^3	10^5
1. Cost estimation to reach TRL5 based on cost estimation according to the following pattern: - Single engineering project and validation: <0.5 Mio€ <1 Mio€ <2 Mio€ - Joint engineering and research project of 2-3 partners: <2 Mio€ <5 Mio€ <10 Mio€				
2. Assumes a 200 l bioreactor volume.				
3. Biological reactors based on commercial systems made of PEEK and operated with electricity for stirring and heating.				
4. ND indicates no data available for this process.				

3.7.5. Feasibility evaluation

The feasibility of bioadhesive production and recycling is based on the entire life cycle for the C2C process. Bio-production of adhesives is in its infancy and considerable research is needed to bring it to a wide spread commercial scale.

Table 14: Feasibility of bioadhesive production and recycling

Adhesive Production	Experts[1] surveyed	Lunar[2] TRL	Current[2] TRL	Future[2] TRL	Comple-xity	Effort	Total Score
lipids/FA							
algae	5	1	4	5	3	2	20
bacteria	4	1	3	5	3	2	18
polysaccarides							
algae	5	1	4	5	3	4	22
bacteria	5	1	4	5	3	3	21
Recycling							
Solvolysis	4	1	5	5	2	2	19
Co-solvent	2	1	2	2	3	2	12
Biodegradation	1	1	1	2	2	2	9
1. Answers from 4 of 12 experts in either a written or telephone survey, added to our opinions.							
2. Scores range from 1 = unfavorable to 5 = favorable. Total score maximum is 30 points.							

3.8. Space equipment materials implication

SMC Concept applied to Lunar S. Pole

A scenario for the SMC concept at the Lunar South Pole will consider production and recycling of CFR-PEEK. Adhesives will not be included because the State of Art is lagging that of plastics and carbon fiber processes. The goal of SMC is automated processing of new components by recycling space craft materials and producing virgin biomaterials that can augment spent materials. Specifically,

- Biomaterial production to feed manufacturing of new components.

- Recycled spacecraft materials augmented with new biomaterials to achieve manufacturing criteria.

- Automated system with sensors and controllers to achieve high yields, superior quality (e.g. FTIR used to check polymer quality).

SMC Considerations

- CRP-PEEK resists to cosmic radiation and has low secondary emission. Ideal for lunar materials.

- CFR-PEEK structure could house AM manufacturing processes and heterotrophic bioreactors.

- Commercially produced PEEK bioreactors a reality and suited for photo-bioreactors with autotrophic organisms.

- Combining PV modules with FP algal bioreactors and Glazes to bandpass UV and visible radiation. Provides decentralized system that adds to flexibility, but would require temperature control.

- Maximum electricity demand per bioreactor is 300 MJ/d or 83 kWh/d (a 4 kW PV panel gives >20 kWh/d, and so the process would require 4 panels).

SMC Production

- Bioreactors to produce bisphenolates (PEEK precursor) and processing PEEK. O_2 byproduct stored and used for other processes.

- Bioreactors to produce propylene (CF precursor) and processing CF. O_2 byproduct production stored and used for other processes.

- PEEK and CF biomaterials would be AM manufactured into components.

The bio-processing concept is illustrated in Figure 12.

SMC Recycling

- Bioreactors coupled to Solvolysis batch reactor to recover polymers of PEEK, CF fibers, and some nutrients from spacecraft and lunar processed biomaterials.

- Pyrolysis for EOL and contaminated CFR-PEEK and CO_2 stored and used for photo-bioreactors (autotrophic) and other processes. Note that s the sole source of carbon for photosynthetic systems. Input of CO_2 is based on the balanced growth rates, giving an algae molar ratio of carbon to nitrogen to phosphorus of 106:16:1, which accounts for the high mass loading to the photobioreactors.

- To enhance degradation for recycling, spacecraft parts could be stored exposed to solar radiation on Lunar surface and processed as needed.

The bio-recycling concept is illustrated in figure Figure 13.

Figure 12 depicts biomaterial production and links to recycling. The sequential steps are:

1) 200 L photo-bioreactors exposed to visible light will produce algal oil and sugars (O_2 byproduct). Oil will be dehydrogenated by catalysts producing propene (H_2O, H_2 byproducts). Each photo-bioreactor will give 1 L/d of oil (about 1100 g) and 2000 g of spent biomass (based on 3300 g algae and nutrients: 6050 g CO_2, 913 g nitrate and 57 g phosphate, plus other trace nutrients). Algae will also produce 1 L/d glucose for fermentation to hydroquinone. 13 kWh/cycle.

2) 968 g propene is acid quenched and distilled to acrylonitrile (H_2O byproduct).

3) To produce CF, 950 g acrylonitrile is mixed with 70 g methyl acrylate and catalysts in a furnace heated to 3000°C without O_2. (5 L x 3000°C)/(1680 x 1h) = 9 kWh/cycle.

4) Recycled CF is added and 910 g CF washed and stretched. Heated 1 hour at 200°C in air (O_2 from photo-bioreactors in step 2) to enhance bonding. 0.6 kWh/cycle.
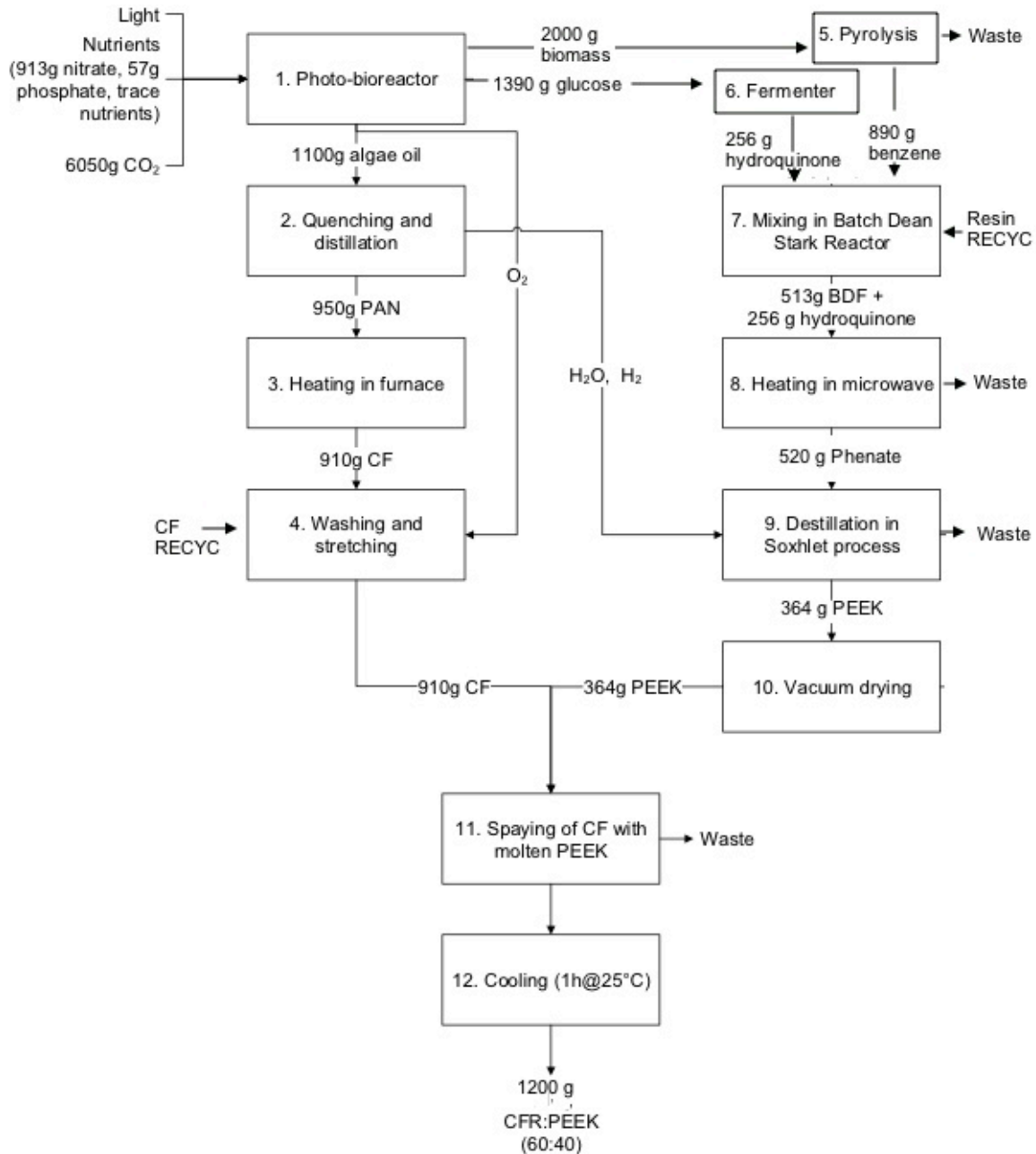

Figure 12: Biomaterial production and links to recycling

5) Spent biomass (2000 kg) not used for oil will be converted to 880 g benzene via pyrolysis then reacted with other precursors to give 513 g of 4,4'-difluornbenzopheneone (BDF).

6) Fermentation of 1390 g of D-glucose to 295 g quinic acid will produce 256 g hydroquinone. Recycled resin precursors added.

7) Batch Dean Stark Reactor to mix 4,4'-difluornbenzopheneone with hydroquinone. 4 kWh/cycle

8) Microwave heated to 100°C for 20 minutes producing PEEK. 14 kWh/cycle.

9) Phenate distilled in Soxhlet process at 120°C for 15 minutes.

10) Heated to 180°C for 18 hours. Cooled to 25°C in water (from dehydration reactions in step 2) to precipitate 364 g of PEEK.

11) a 60:40 for CF:PEEK ratio is made by spraying CF with PEEK giving a CFR-PEEK product ready for manufacturing, 0.5 kWh.

12) CFRP cooled for 1 hour at 25°C and then ready for manufacturing.

Total power demand for biomaterial production 41 kWh/cycle, assuming some low temperature heating and cooling can be achieved via heat exchange with the outside environment.
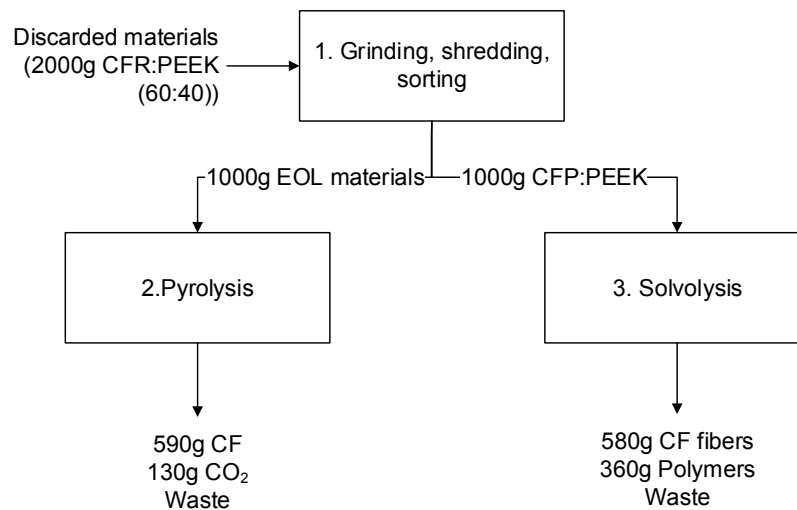

Figure 13: Recycling concept for space craft with 60:40 CFR-PEEK content

Figure 13 depicts a recycling concept for space craft with 60:40 CFR-PEEK content. The steps are:

1) Discarded spacecraft and other waste materials.

2) Spacecraft ground, shredded and sorted.

3) Pyrolysis of 1 kg CFR-PEEK to recover 99.8 of CF or 0.6 kg CF / kg waste with 0.13 kg CO_2 as a byproduct* and 0.59 to 2.0 kWh/kg waste.

4) Solvolysis of 1 kg CFR-PEEK with GRAS (80% Ethanol from photo-bioreactor step 2) to recovery 98% of CF (0.59 kg) and 90% of PEEK precursors (0.36 kg). Same as pyrolysis with 2.0 kWh/kg waste.

*Assumes 30% CO_2/kg PEEK emissions gives 0.24 kg/kg CF-PEEK (based on 0.2% CF loss x 60% CF + 33% x 99.8% resin loss x 40% resin= 0.12+0.3x0.399 kg/kg). Decomposition of PEEK to CO, CO_2 and phenol (about 30% each)