Activity # 3 Updates:

Zero-Waste Process for Conversion of Wet Greenhouse Wastes and Agro-Forestry Residues into Recycled Water/Bioenergy/High-value Bioproducts

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Collaborating with Western Maple Bio Resources Inc.

May 5, 2022

Webinar

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Acknowledgement

- Government of Canada under the Canadian Agricultural Partnership
- Biomass Cluster holder: BioFuelNet Canada
- **Partners**: Western Maple Bio Resources Inc. (WMB), Western University, Mucci Farms, Elimira's Own greenhouse farm.

Goal Statement

- Valorization of biomass (in particular, wet greenhouse waste, crop residues or forestry residues) for generation of **recycled water, bioenergy and various high-value bioproducts**, to reduce GHG emission, and strengthen sustainability and bioeconomy of Canadian agriculture and agri-food sector as well as forestry sector.

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Project Overview

- **Project Objectives**:

(1) Develop **an innovative zero-waste technology** to convert greenhouse waste and agricultural/forestry residues to various high-value bioproducts (e.g., **bio-based hydroponic foams** for seedling germination and plant cultivation, **bio-based formaldehyde-free wood adhesives,** and **bio-based super absorbent polymers (SAPs)** for agricultural soil water retention, etc.), while recycling water and bioenergy. Vote 10

(2) Demonstrate **the applications** of bio-based hydroponic foams and bio-based SAPs in greenhouse, and the **bio-degradability** of these biomaterials. Vote 1

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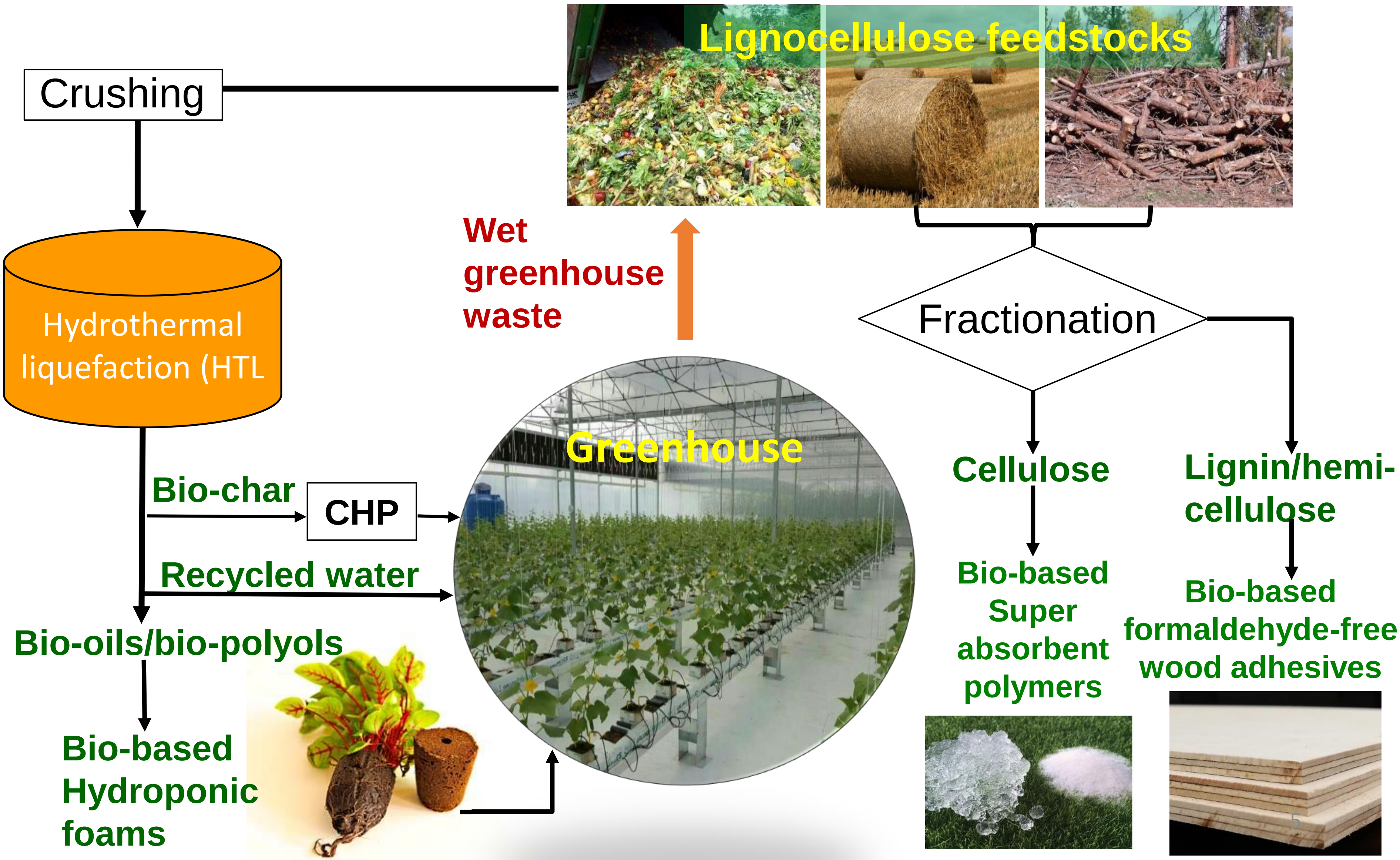
1 - Approach

Zero-Waste Process for Conversion of Wet Greenhouse Wastes and Agro-Forestry Residues into High-value Bioproducts



2 - Technical Accomplishments/ Progress/Results

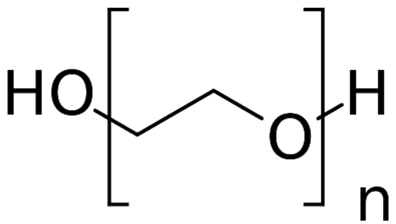
Deliverable 1:

Demonstration of a cost-effective and scalable hydrothermal liquefaction (HTL) process for direct conversion of wet greenhouse wastes (no need of de-watering or drying), agricultural/forestry residues into bio-oils, bio-char and recycled water. **(Status: 100% completed).**

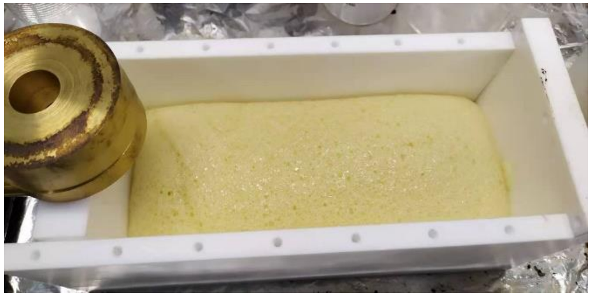
- Developed environmentally friendly and cost-effective depolymerization of lignin to produce bio-polyols/phenols using hydrogen peroxide at ambient conditions;
- Conducted HTL runs using cornstalk-water slurry 1.5 kg/h on the system built, achieving 35% oil (bio-polyols) yield, and approx. 85% biomass conversion;
- Completed HTL of agricultural/forestry residues in a scale of 5 kg/batch for more than 4 batches.

Deliverable 2:

The bio-oils produced from HTL of wet greenhouse wastes with/without cornstalk were successfully used to substitute 100% petroleum polyol in the synthesis of bio-based polyurethane (BPU) hydroponic foams and the foams have been tested for seed germination/planting applications. The biodegradation tests on the BPU foams have also been completed. **(In progress, 80% completion).**



PEG – petroleum-based polyols



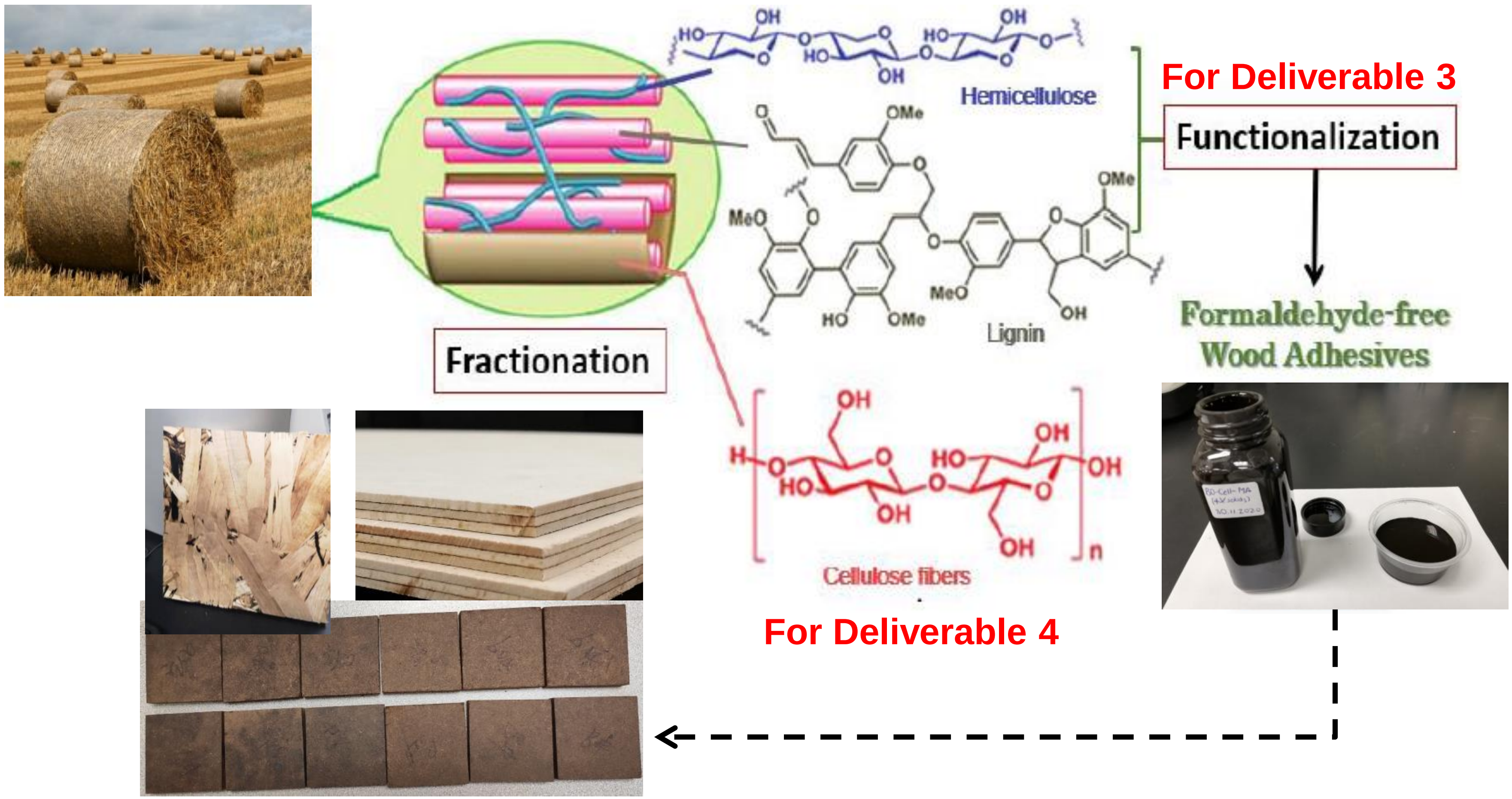
Petroleum-based PU foam (reference)

Bio-polyols

BPU hydroponic foams

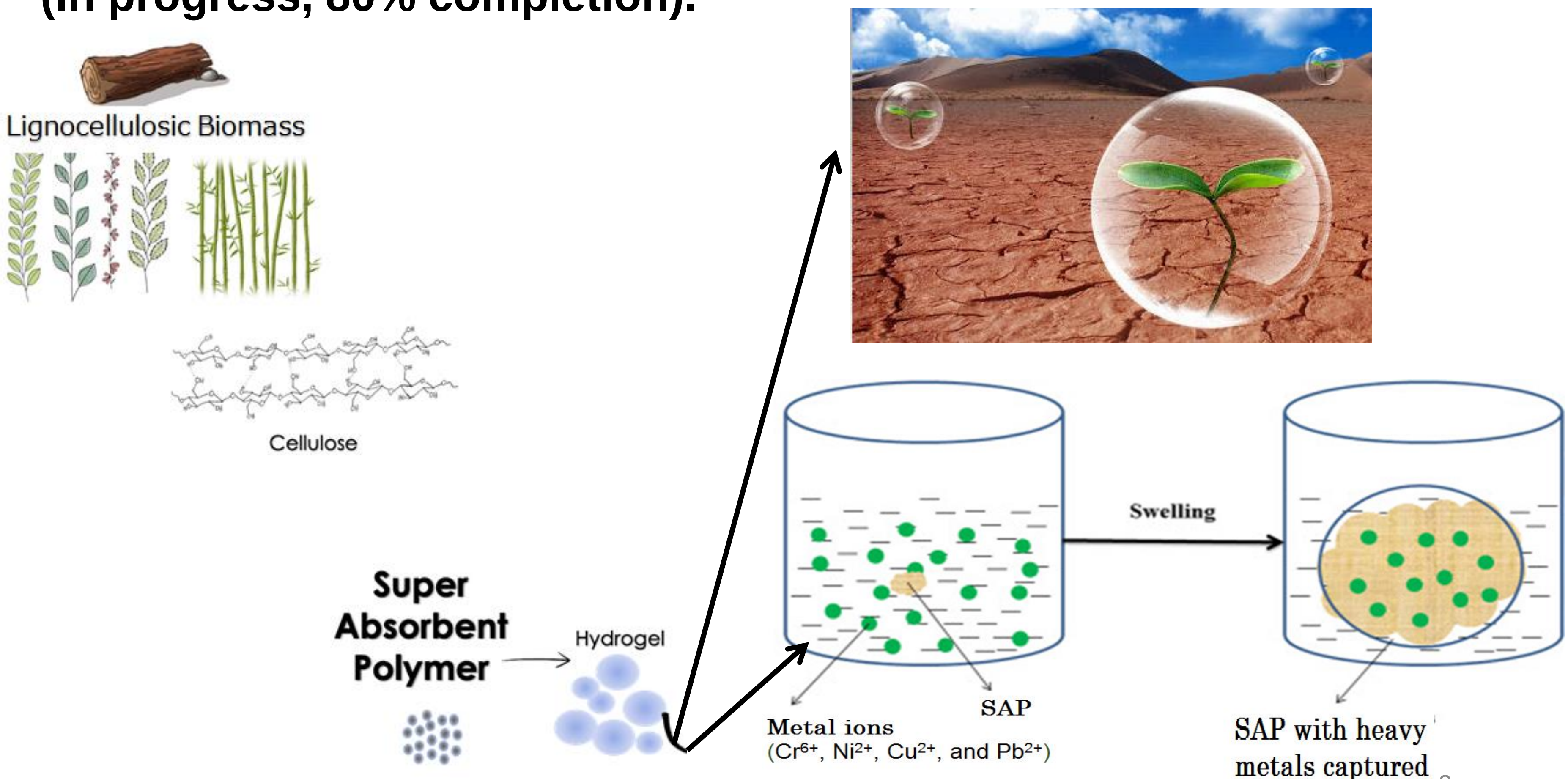
Deliverable 3:

Crop residue was effectively fractionated into lignin/hemi-cellulose and cellulose fibers by organosolv pulping method under mild conditions. The obtained lignin fraction was converted into bio-based formaldehyde-free (BBFF) wood adhesives, successfully applied for plywood, fiberboard and OSB manufacture, achieving good bonding strength and superb water resistance. **(In progress, 90% completed).**



Deliverable 4:

Conversion of agricultural bio-resources (starch, cellulose, crop-residue-fractionated cellulose) into bio-super absorbent polymers (Bio-SAPs), and application of bio-SAPs for agricultural soil water retention application (attaining 100-200 water absorption capacity) and removal of heavy metals. **(In progress, 80% completion).**



Deliverable 5: (Vote 1)

The biodegradability of the BPU foams have been studied by incubation with *Dyella* sp. for a period of 8 weeks. The weight loss, Fourier-transform infrared (FTIR) spectra, thermogravimetric analysis (TGA) results, and scanning electron microscopy (SEM) images of foam samples were collected and analyzed. The BPU foams exhibited much better biodegradability than the petroleum-based polyurethane (PU) **(100% completion).**

Original Article

Biofuels Bioproducts & Biore

Production of bio-polyurethane (BPU) foams from greenhouse/agricultural wastes, and their biodegradability

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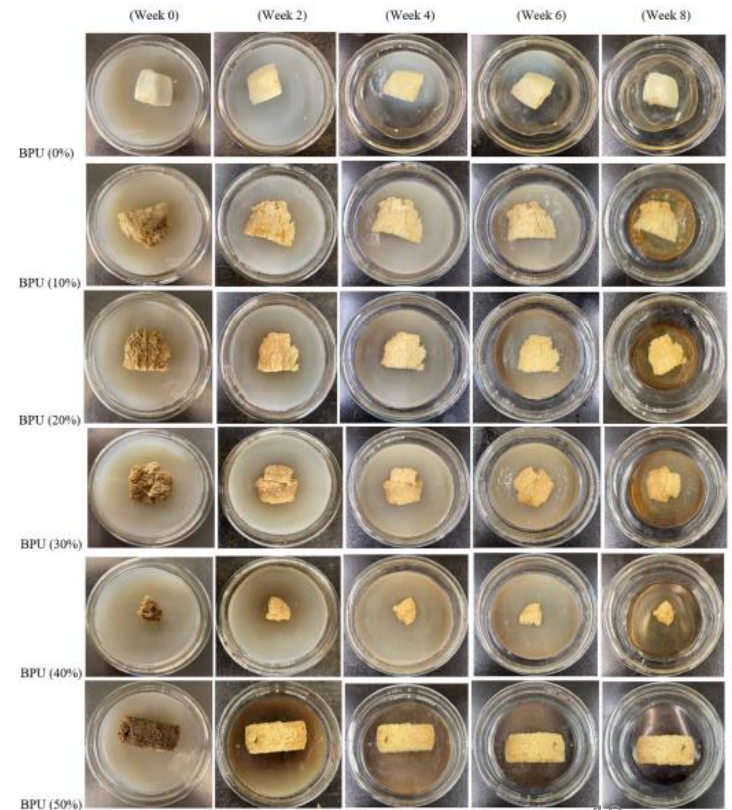
Received October 21 2021; Revised December 18 2021; Accepted January 14 2022;
View online at Wiley Online Library (wileyonlinelibrary.com);
DOI: 10.1002/bbb.2344; *Biofuels, Bioprod. Bioref.* (2022)



Images of PU/BPU foams after degradation by *Dyella* sp. for various periods.

Deliverable 2:

- **Conversion of Agricultural and Greenhouse Wastes into Bio-based Hydroponic Foams**

Hongwei Li[1], Charles Xu[1], Ze-Chun Yuan[2]

Background

- Greenhouse wastes, including the leaves, stems, and vines of greenhouse plants, are abundant renewable resources with more than 2 million hectares of greenhouses all over the world
- Greenhouse wastes are usually disposed by landfill or simply by dumping them in dry ravines or open spaces, leading to uncontrolled burning, blockage of riverbeds, poisoning of cattle and sheep, and causing a visual blight on the landscape

Background

- Polyurethane (PU) is popular as packing, insulation, bedding, and cushion materials

- The global PU foam market was projected to grow from USD 37.8 billion in 2020 at a compound annual growth rate (CAGR) of 7.5% to USD 54.3 billion by 2025

Background

- Conventional PU foam is heavily fossil-dependent because the two major components, polyols and isocyanates, are both derived from fossil resources.

- As reported by Research and Market, the market for BPU foam was around 27 kilotons in 2020 and the market is expected to grow at a CAGR of more than 3.5% in terms of volume to 2026.

Background

- Hydroponic PU foams, are the top 17 best growing media for soilless cultivation

- Hydrothermal liquefaction or simply liquefaction has been applied as a cost-effective conversion technique to convert biomass into liquid products known as biocrude oils or bio-oils/bio-polyols that can be used directly for synthesis of bio-based polymer materials

Motivation:

If liquefied greenhouse wastes were used for the preparation of bio-based PU (BPU) foams, particularly hydroponic PU foams for soilless cultivation, it would significantly boost cyclic economics of greenhouse wastes, increasing the added value of greenhouse wastes and lowering disposal costs.

Approaches:

Greenhouse wastes are mainly composed of three major components (cellulose, hemicellulose, and lignin), all containing hydroxyl groups in their structures. Through liquefaction treatment, the three major components are decomposed/de-polymerized into oligomers (bio-oils or bio-polyols) with active hydroxyl groups, which were used as alternative to petroleum-based polyol for the preparation of BPU foams.

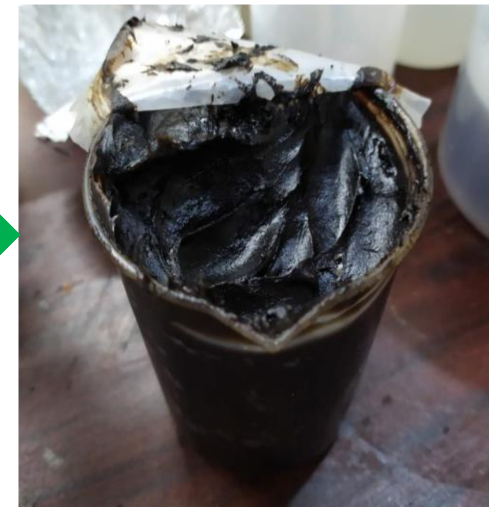
Methodologies

BIO-OIL (BIO-POLYOL) PRODUCTION

HYDROPONIC PU FOAM PREPARATION

GREENHOUSE TEST

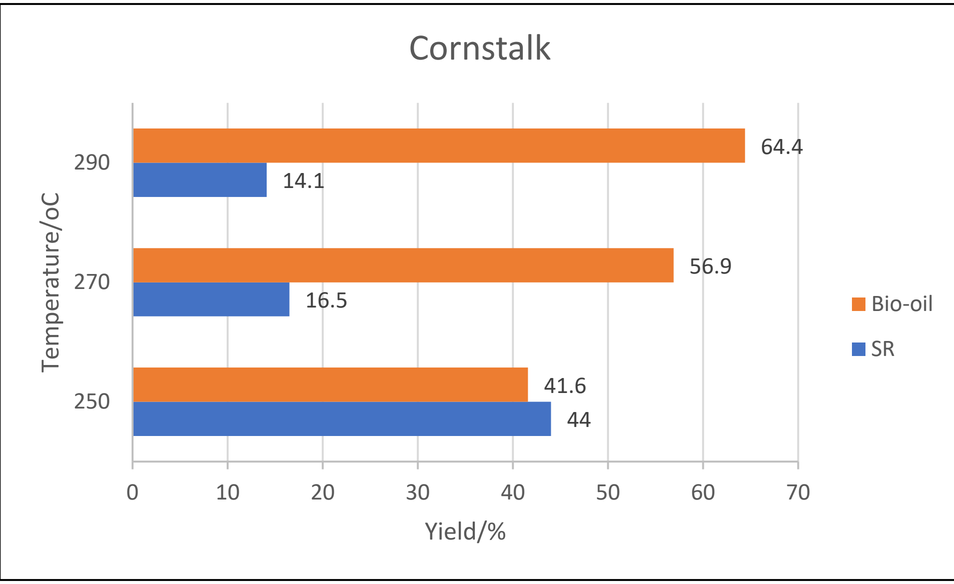
Bio-oil (Bio-polyol) Production

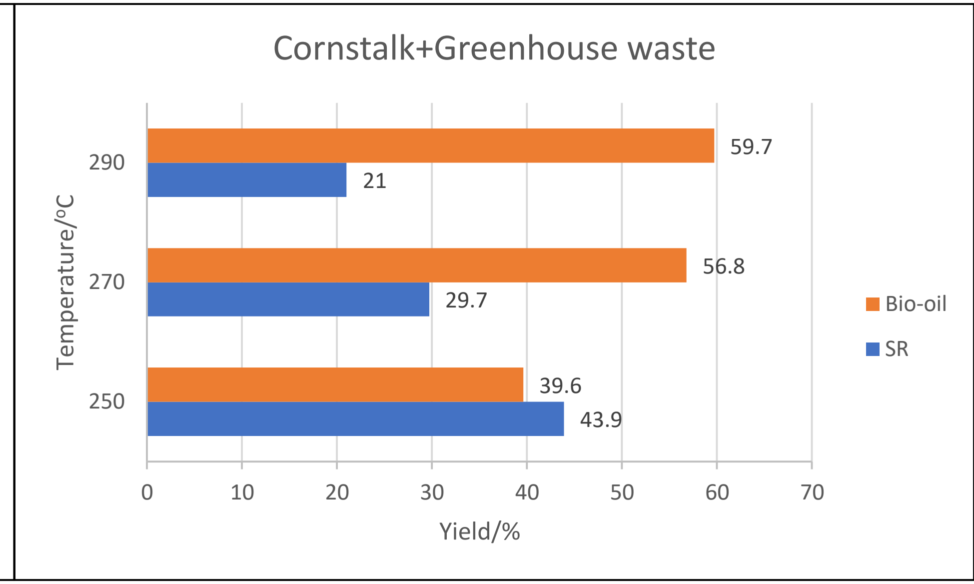


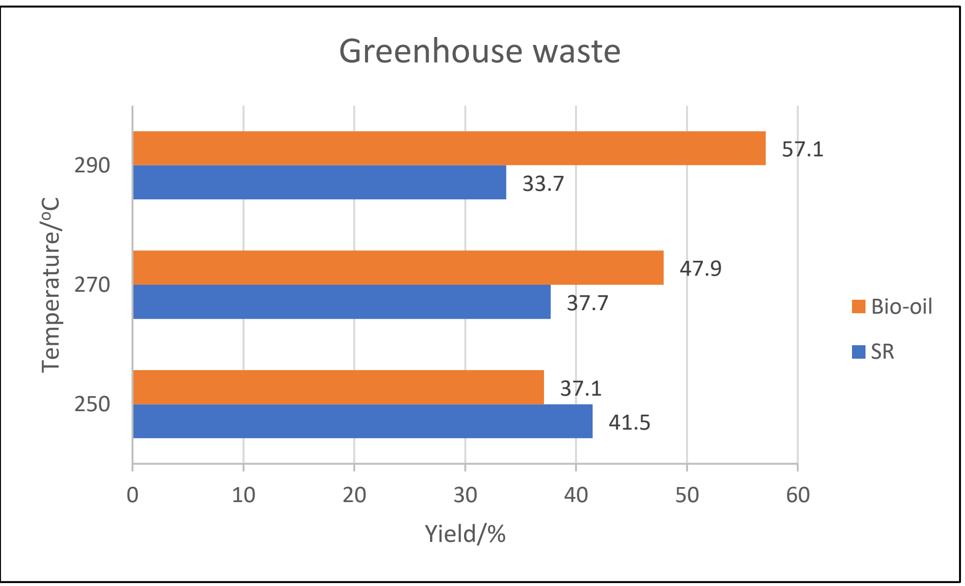
Agricultural & greenhouse waste

Liquefaction process

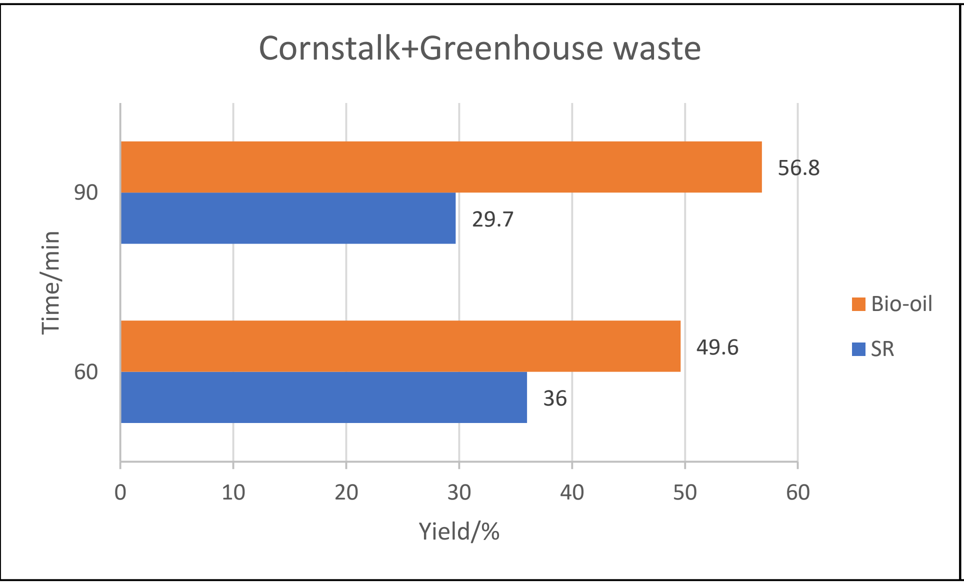
Bio-oil (Bio-polyol)

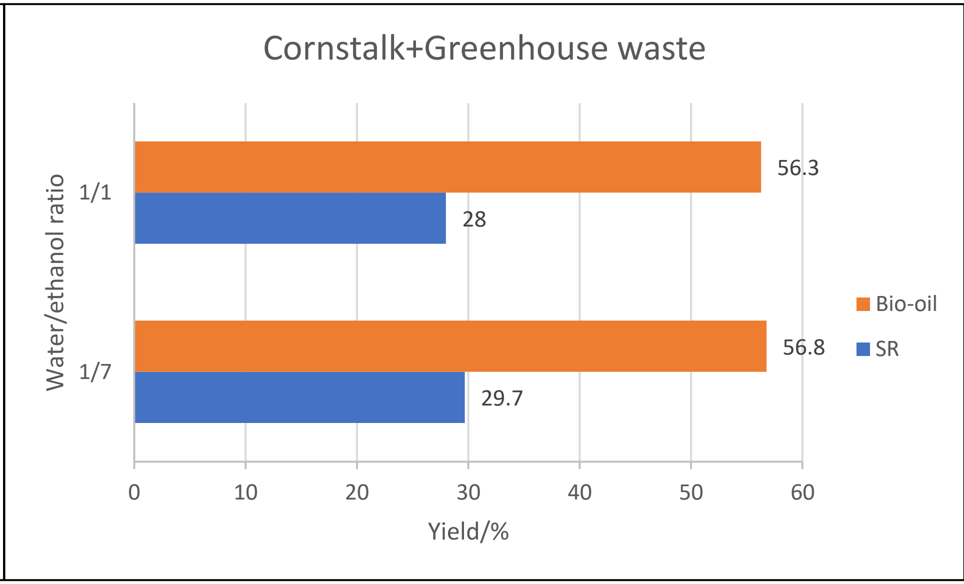


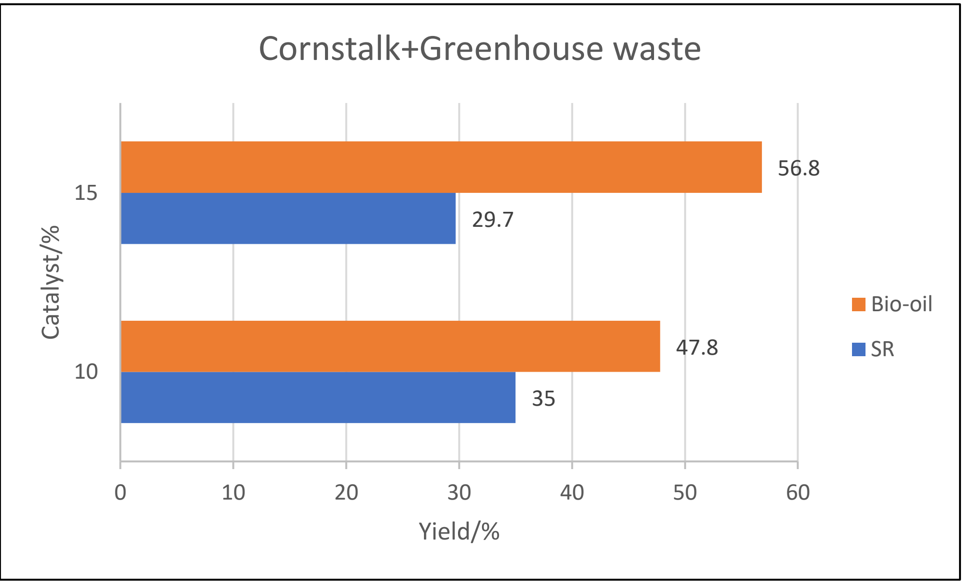




Even though the best temperature for liquefaction of cornstalk or greenhouse waste or their mixtures was 290 ºC in terms of the highest oil yield, 270 ºC was determined taking energy cost into account.







Conditions: **20%** biomass, **10%** ethanol, **70%** water, **15%** NaOH, **1.5 h** at **270 ºC** (16 L reactor).

Table 1. The properties of bio-oil from cornstalk and greenhouse waste liquefaction.

Bio-oil properties	Bio-oil
Oil yield (%)	56.3
Hydroxyl number (mg KOH/g)	534
Viscosity (Pa·s)	1.4
Mw (g/mol)	998
Mn (g/mol)	470
PDI	2.1

Hydroponic BPU foam preparation

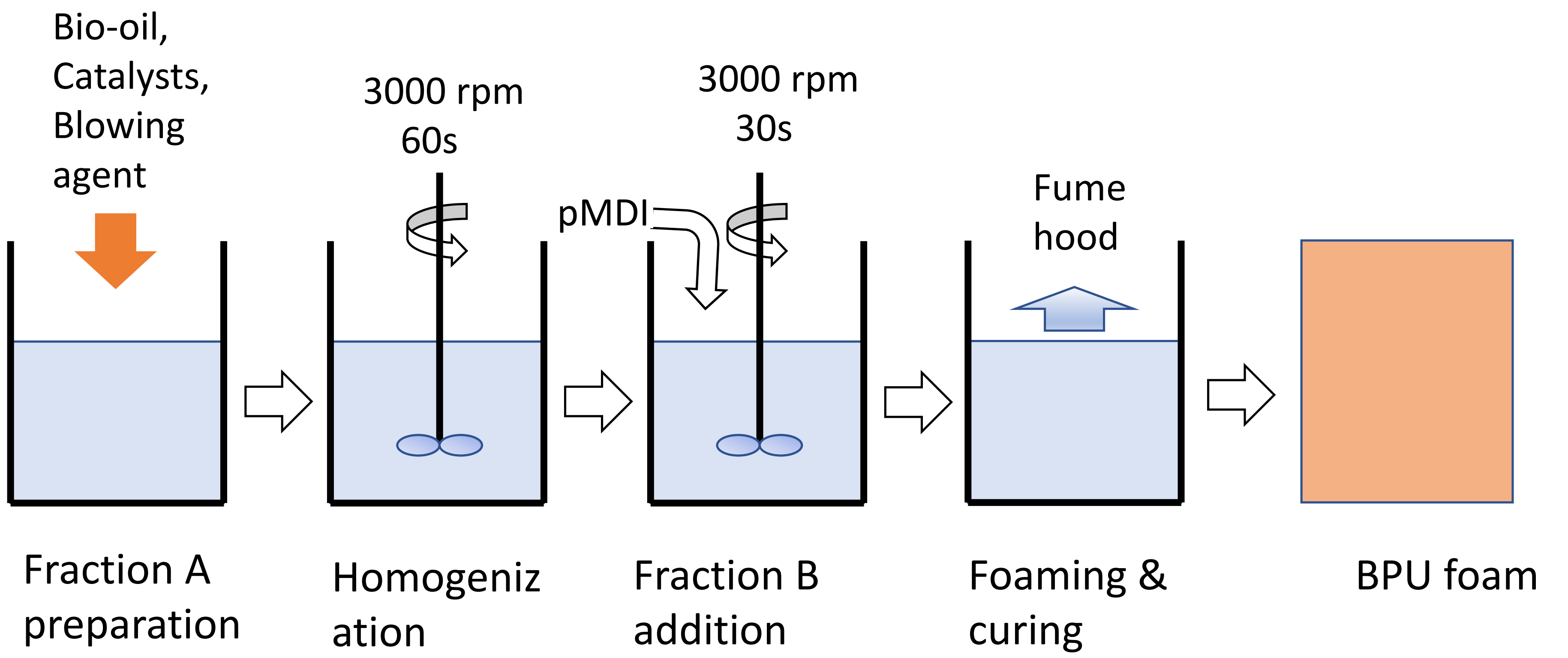


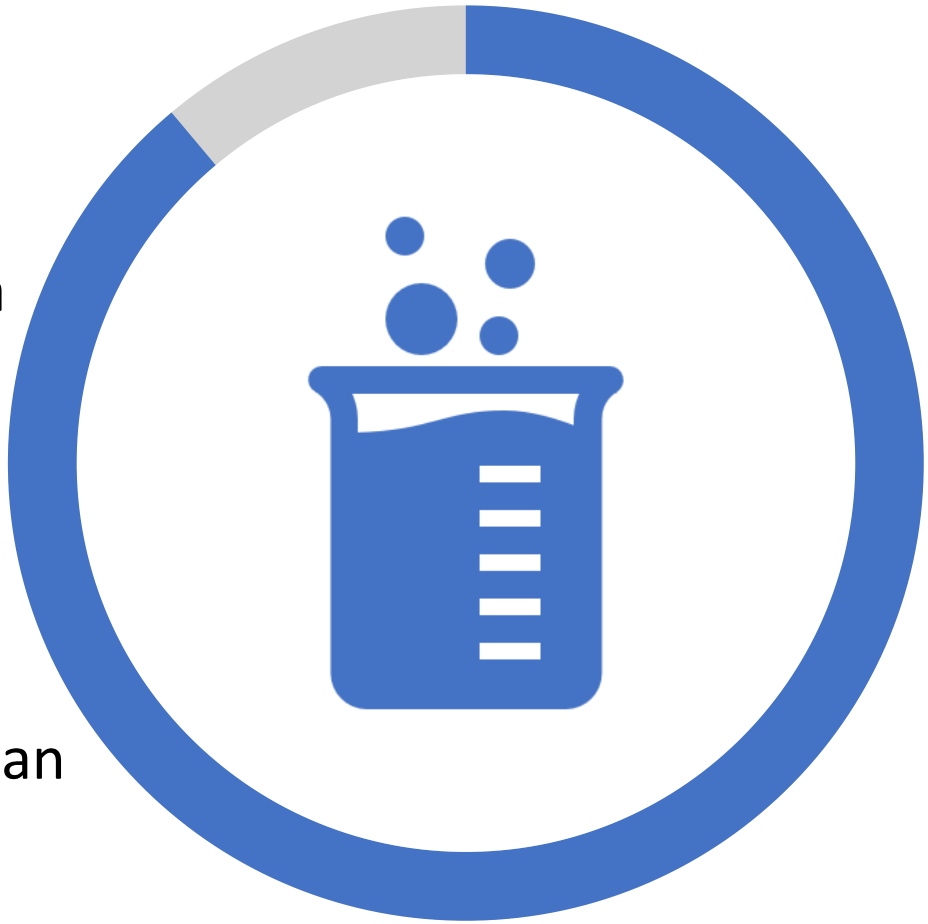
Table 2. Physical properties of BPU foam samples.

FOAM ID	DENSITY/ (KG/M^3)	OPEN CELL CONTENT/%	WATER ABSORPTION CAPACITY/%
1	95.3	61.3	504.8
2	46.3	59.3	1031
3	283	59.7	117
4	258	48.5	130
5	69.1	86.4	552.4
6	117.4	79.6	519.6
7	166.2	94.3	321.5
8	51.7	59.3	746
9	49.9	54.3	737
10	32.3	69.2	1269.3
11	**42.2**	**88.9**	**1327**
12	62.6	66.7	627.6
13	115.9	78.3	233

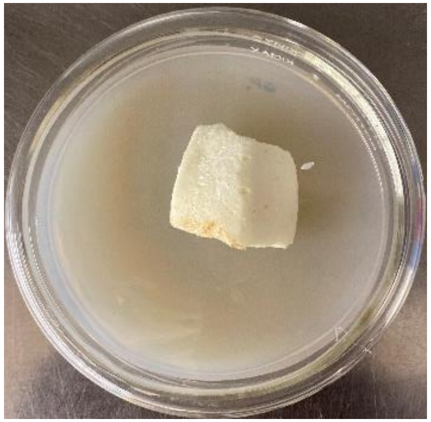
- As shown in Table 2, most of the prepared BPU foam samples had densities in the range of 30~170 kg/m^3, indicating the viability of planting.

- The optimal foam recipe resulted a foam with ~89% open cell content, which is essential for oxygen infiltration.

- The optimal foam has a high water absorption capacity, suggesting it can absorb enough water for plant growing.



Biodegradation experiments

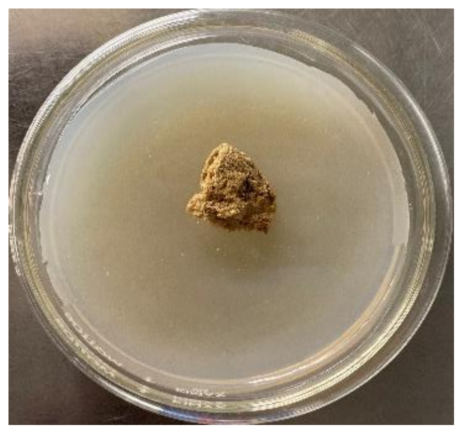


0% BPU

10%BPU

20%BPU

30% BPU



40%BPU

50%BPU

Figure 1. BPU foams degradation by selected bacteria for 8 weeks.

Biodegradation experiments

All bio-based PU foam samples prepared with wet greenhouse wastes and agricultural residues exhibited better biodegradability than reference foam prepared with petroleum polyol.

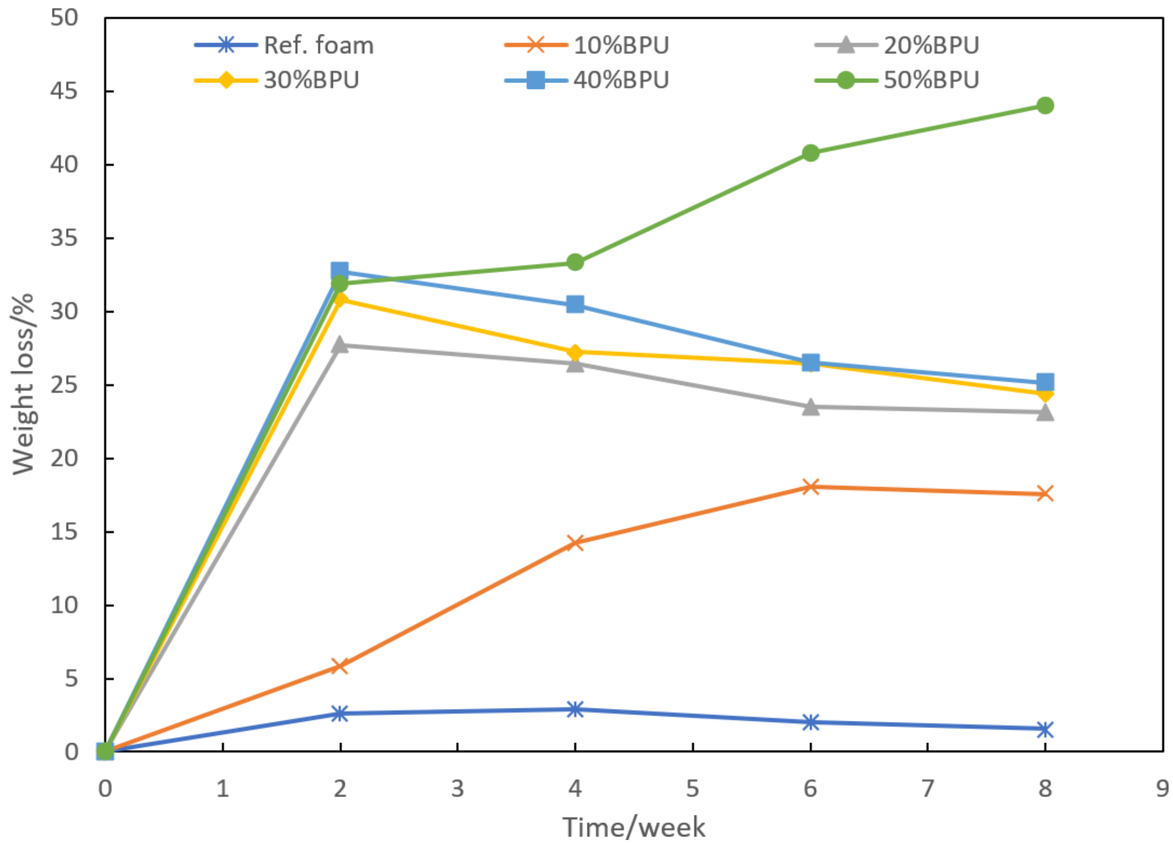
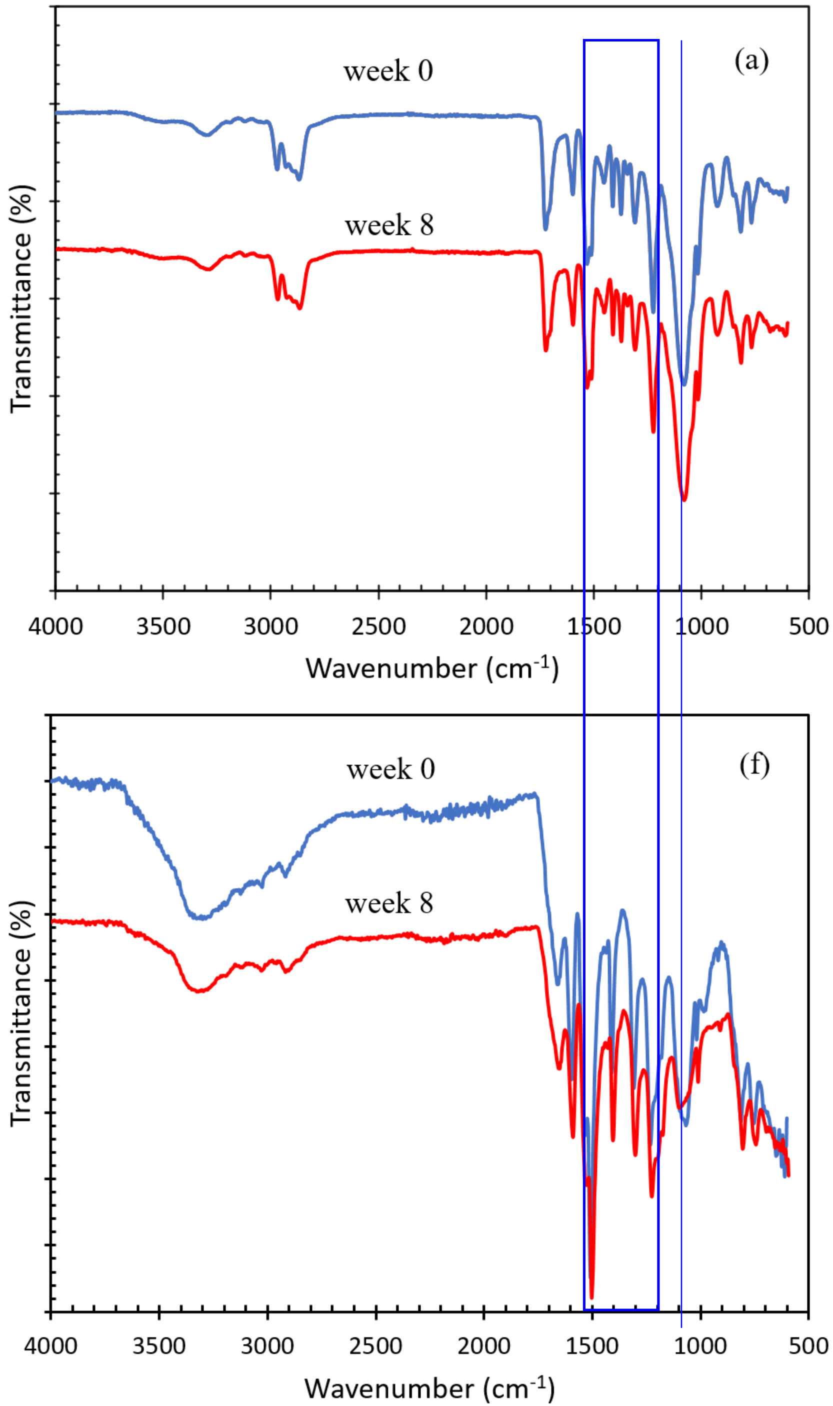


Figure 2. Influence of incubation time on weight loss of bio-based PU hydroponic foam (BPU 0-50%) samples.



Decrease in intensity of peaks (1172 cm^{-1}, 1500-1230 cm^{-1}) were observed, which were likely caused by the hydrolysis of ester, ether, and urethane bonds in the foam structure, and loss of other unstable functional groups.

Figure 3. FTIR spectra of the reference foam (a), 50%BPU (f) before and after inoculation with *Dyella sp* for 8 weeks.

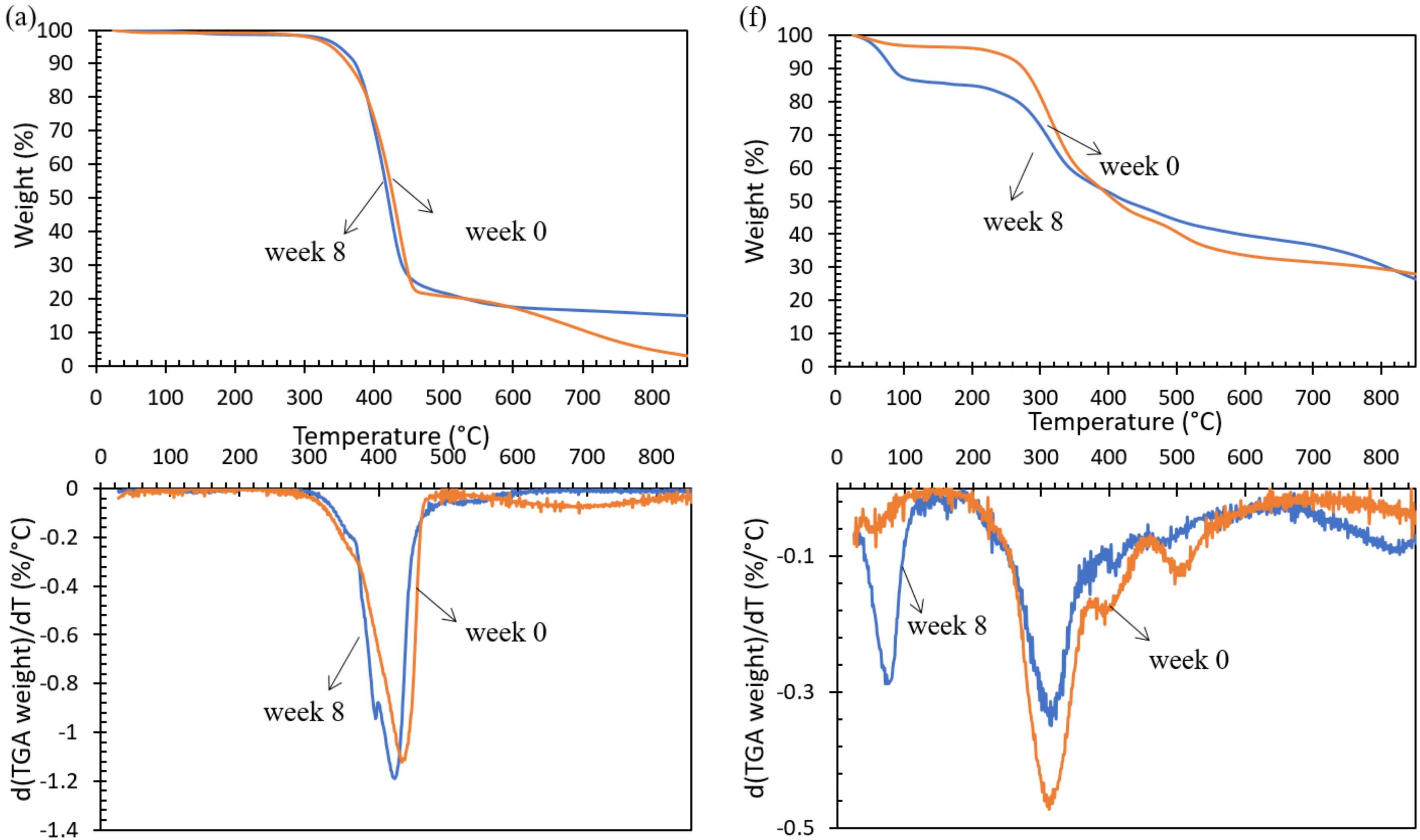
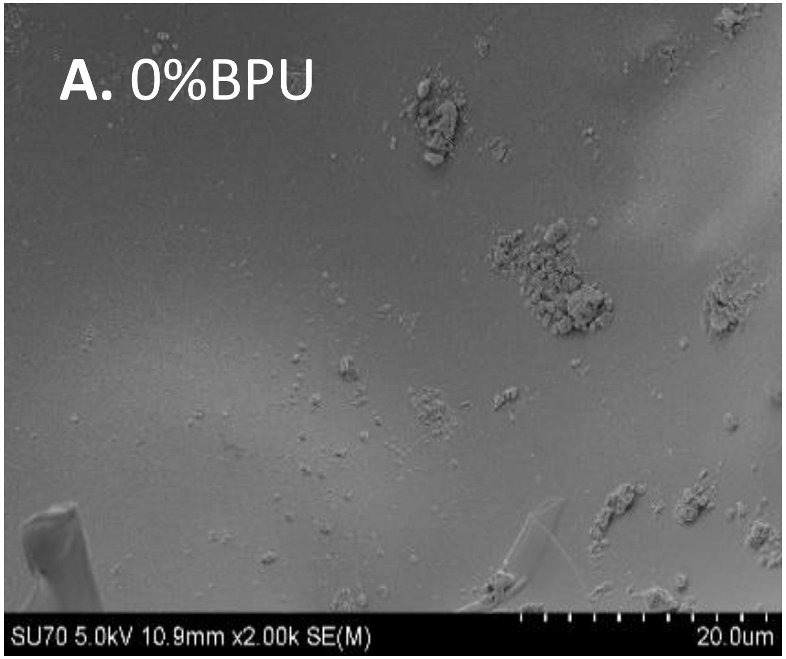
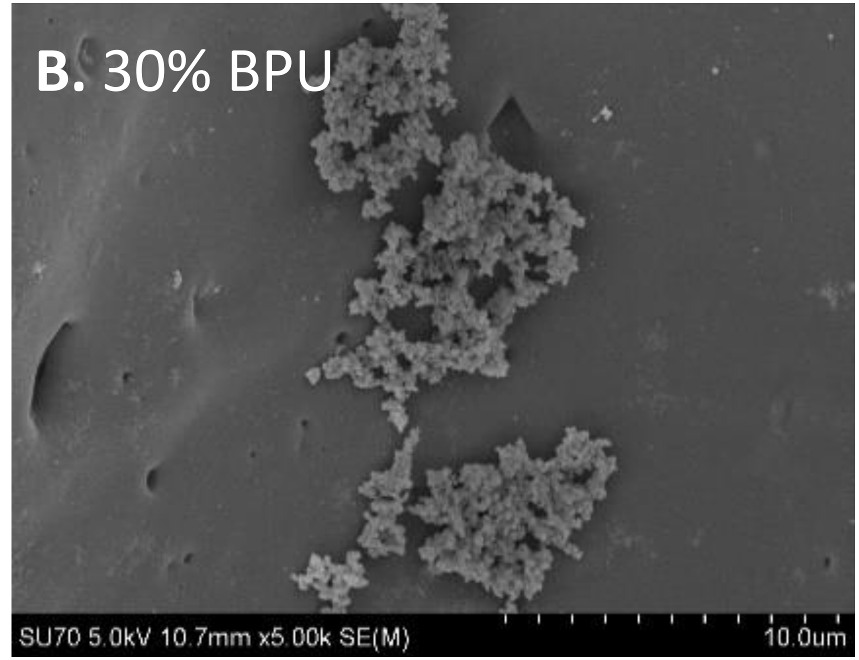


Figure 5. TGA/DTG plots of the reference foam (a), and 50%BPU (f) foams before and after inoculation with *Dyella sp* for 8 weeks.

Comparing with those at week 0, all BPU foams at week 8 are relatively less thermally stable and started to degrade at a lower temperature.





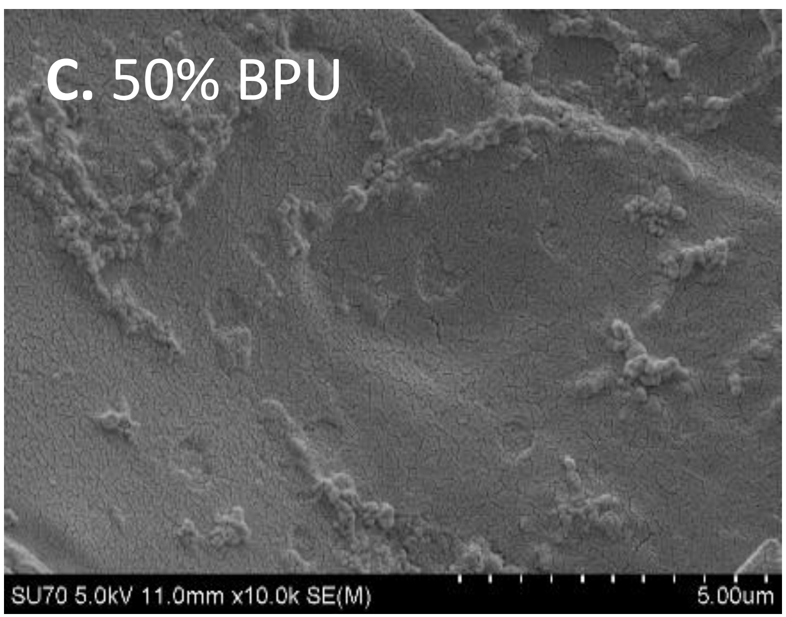
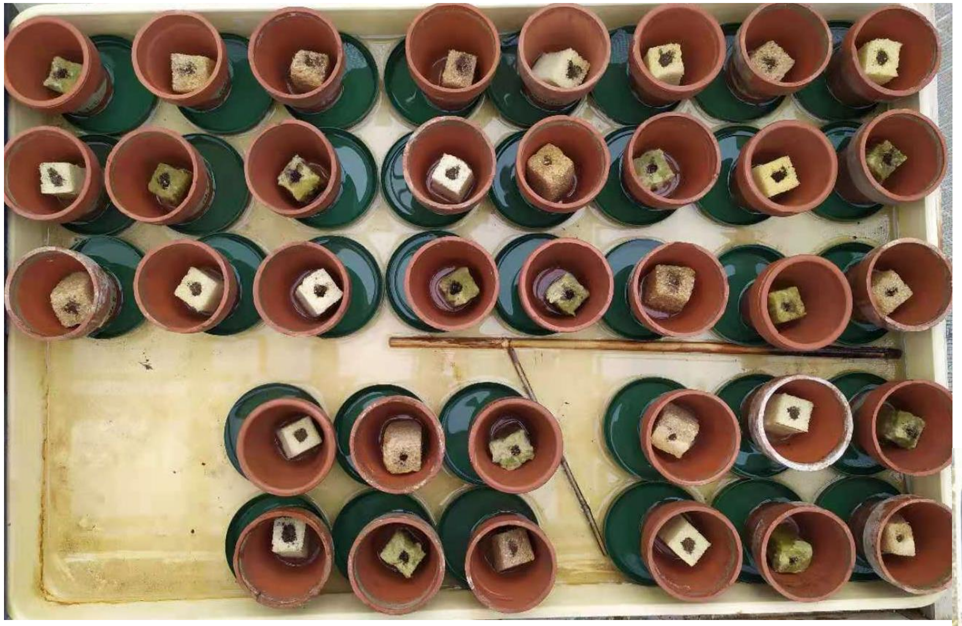


Figure 6. SEM micrographs of BPU (0%, 30 and 50%) foams after degradation by bacteria for 8 weeks:
(A): Exterior surface of PU 0% with a weak biofilm-forming capacity of bacteria;
(B): Exterior surface of BPU 30% with a strong biofilm-forming ability of bacteria;
(C): Interior of BPU 50% with bacteria.

Seed Germination Tests



Rock wool (commercial germination material)

Petroleum-based PU foam (self prepared)

BPU foam (derived from agricultural & greenhouse waste)

- Germination rate: Commercial foam: 87%
  PU foam: 30%
  BPU foam: 17%
- Emergence rate： Commercial foam: 87%
  PU foam: 27%
  BPU foam: 13%

Reasons for germination test failure:

- BPU foam property: have a very long water absorption time (>10 min to get a full wetness of foam body);
- Error: due to the high vaporization of water at a high room temperature (greenhouse), did not keep the seed moist, resulting in the seed being killed after breaking dormancy.
- System error.

Plant growing test

(Shouguang Company, CHINA)

Day 1

After one month

The root did not develop successfully!

Directions to improve:

- Improve open cell content
- Decrease foam mechanical properties
- Increase bio-oil content

Table 3. Physical properties of BPU foam samples from modified recipes.

Foam ID	Density/kg/m^3	Open cell content/%	**Water absorption time**	Water absorption capacity/%
1	172.5	77.6	32sec7	479.2
2	240.6	70.5	10sec85	278.1
3	126.5	78.2	15s97	607.8
4	121.3	77.4	12s61	409.2
5	147.0	75.2	7s13	483.7
6	145.6	57.9	1min33sec42	427.9
7	192.8	64.4	14s58	357.2
8	176.1	47.3	2min46s86	188.7
9	157.7	61.9	55s86	600.4
10	29.3	89.2	2min14s28	531.6
11	213.1	80.0	3s85	274.6
12	130.7	79.7	19s23	353.5
13	163.4	66.1	15s88	430.8
14	92.8	88.9	26s49	436.3
15	85.8	69.6	11s95	523.8
16	141.6	79.7	7s59	420.6

Water absorption time can be as short as 8 seconds, indicating the foam body's rapid wetness upon contact with water.

Even though the density increased, it’s still within the range of 20~200 kg/m^3 (NY/T 2118-2012) for soilless growing media.

The optimal foam sample had an open cell content of ~70%, 10% higher than the requirement (NY/T 2118-2012) for soilless growing media.

Optimal foam mechanical properties

* After water absorption for 3 days and dried.

Table 4. Mechanical properties of commercial and BPU foam samples.

Foam ID	**10% compression strength/kPa**	**50% compression strength/kPa**	**Max. stress/kPa**
15	54.0	222.0	248.0
15 (wet*)	24.0	119.0	236.0
Commercial foam	36.7	61.2	101.0
Commercial foam (wet*)	42.0	105.0	114.0

Self-germination Test:

Foam sample

Place seeds in foam media

Sprinkle some soil over the seeds

Wet foam media

Improvements: Foam body can get fully wet in seconds.

Summary:

Efficient liquefaction conditions for agricultural and greenhouse waste were obtained: 20% biomass, 10% ethanol, 70% water, 15% NaOH, 1.5 h at 270 ^{o}C. Bio-oil yielded 56.3%, with a hydroxyl number of 534 mg KOH/g and a molecular weight of 998 g/mol.

Biodegradation test results showed that BPU foams had a better biodegradability than the petroleum PU foam; FTIR, TGA, and SEM results indicated that the efficiency of biodegradability of bio-based PU foams increased as the bio-oil content increased.

Planting experiments shows that our bio-based PU foams derived from greenhouse and agricultural waste had the potential for application in greenhouses.

Summary (Cont'd)

After modification, BPU foam can be achieved with 100% bio-polyol.

The optimal BPU foam sample has the following physical properties: density: 85.8 kg/m^3; open cell content: ~70%; water absorption capacity: ~530%; water absorption time: ~12 s.

The optimal BPU foam sample has the following mechanical properties: 10% deformation compression strength (DCS): 54 kPa; 50% DCS: 222 kPa; max. stress: 248 kPa.

Next step

Time to complete	Project milestones	Activities to complete the milestone	Months needed to complete	Success Criteria
Jun 5	Self Test plant germination; collect enough fresh bio-oil	Self-check if seeds can be germinated, including selection of acids used for neutralization, procedure for foam preparation, pH; grind tomato waste into powder; 2 runs of 16 L liquefaction reaction	2 months	Realizing plant germination test in our lab; obtain 2kg bio-oil
Aug 5	Prepare and send out germination samples to UWO and Shouguang Company respectively	According to self-germination check results, prepare and conduct germination test at greenhouse in UWO and Shouguang Company	2 months	Realizing plant germination test from professional way
Sep 30	Get conclusion from Shouguang Company	Based on the results, make further decision on the project	2 months	Provide industrial information for scale-up
Dec 31	Decrease foam density	Introduce new equipment to further modify foaming process	3 months	Making foam with a density as low as 20 kg/m^3

Activity # 3 Updates:

Charles Xu[1], Hongwei Li[1], Ze-Chun Yuan[2]
[1]Western University,
[2]London Research and Development Centre, AAFC
Collaborating with Western Maple Bio Resources Inc.

3 - Relevance

- This BMC cluster is focussed on advancing the emerging technologies with the potential to revolutionize agricultural production of biomass and residues across Canada, to sustainably meet Canada’s growing need for biomass for fibre and fuel.

Goal of Activity #3 of BMC: Valorization of biomass (in particular, wet greenhouse waste and agricultural/forestry residues) for generation of recycled water, bioenergy and various high-value bioproducts, to reduce GHG emission, and strengthen sustainability and bioeconomy of Canadian agriculture and agri-food sector as well as the forestry sector.

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4 - Critical Success Factors

- **Critical success factors:**
  1) Development of the innovative **zero-waste technology** to convert greenhouse waste and crop residues or other solid wastes to various high-value bioproducts, while recycling water and bioenergy;
  2) **Patenting of 2-3 inventions** evolved from this Activity(1 PCT/US/Canadian patent on bio-based formaldehyde-free wood adhesive filed in 2021;
  3) **2 invention reports** (Cellulose-based SAPs, and Crude cellulose-based concrete water reducers) have been submitted in 2021;
  4) **Training** of more than 10 highly qualifies personnel (HQP) with needed expertise in synthesis and characterization of bioproducts.
- **Major challenges (in commercialization of technologies/products)**:
  1) Technoeconomic viability of the processes developed in our Activity for conversion of biomass into various high-value bioproducts;
  2) Scalability of the processes.

5. Future Work

- **Deliverable 1** (Vote 10): **Scaling up the process to liquefy or fractionate lignocellulosic biomass to produce a large amount of bio-crude oils or bio-polyols or bio-phenols as well as crude cellulose** on a large scale in a continuous-flow reactor (6kg/h)
- **Deliverables 2** (Vote 1 and 10): Demonstrate the application of bio-based hydroponic foams as seed germination/plant cultivation media in greenhouse.
- **Deliverables 3-4** (Vote 10): **Optimize the synthesis processes for other various high-value bioproducts (**BBFF wood adhesives, and bio-SAPs) and their applications.
- **Performing techno-economic studies** to assess the economic viability of the above zero-waste technology including the HTL, fractionation and the synthesis processes for various high-value bioproducts.

Special Acknowledgement of Our Team

- **Dr. Sean Yuan** (Research Associate)
- **Flora Cao** (Research Technician)
- **Dr. Lilly Li** (PDF)
- **Dennise Sosa** (PhD student)
- **Rosa Arredondo** (PhD student)
- **Thahn Vo** (PhD student)
- **Glen Dsouza** (PhD student)

- **Vincent Wang**, **Alicia Zhou** and **Queena Guo** (WMB, Industrial partner)
- **Dr. Wensheng Qin** (Lakehead U, Biology, academic collaborator)
- **Dr. Sheila Macfie**, **Ms. Aixia Wang** (Western U, Biology, academic collaborator)

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Thank you!