DOE Bioenergy Technologies Office (BETO)
2019 Project Peer Review

Multi-stream Integrated Biorefinery Enabled by Waste Processing

03/01/2018
ADO
Integrated Biorefinery (IBR)

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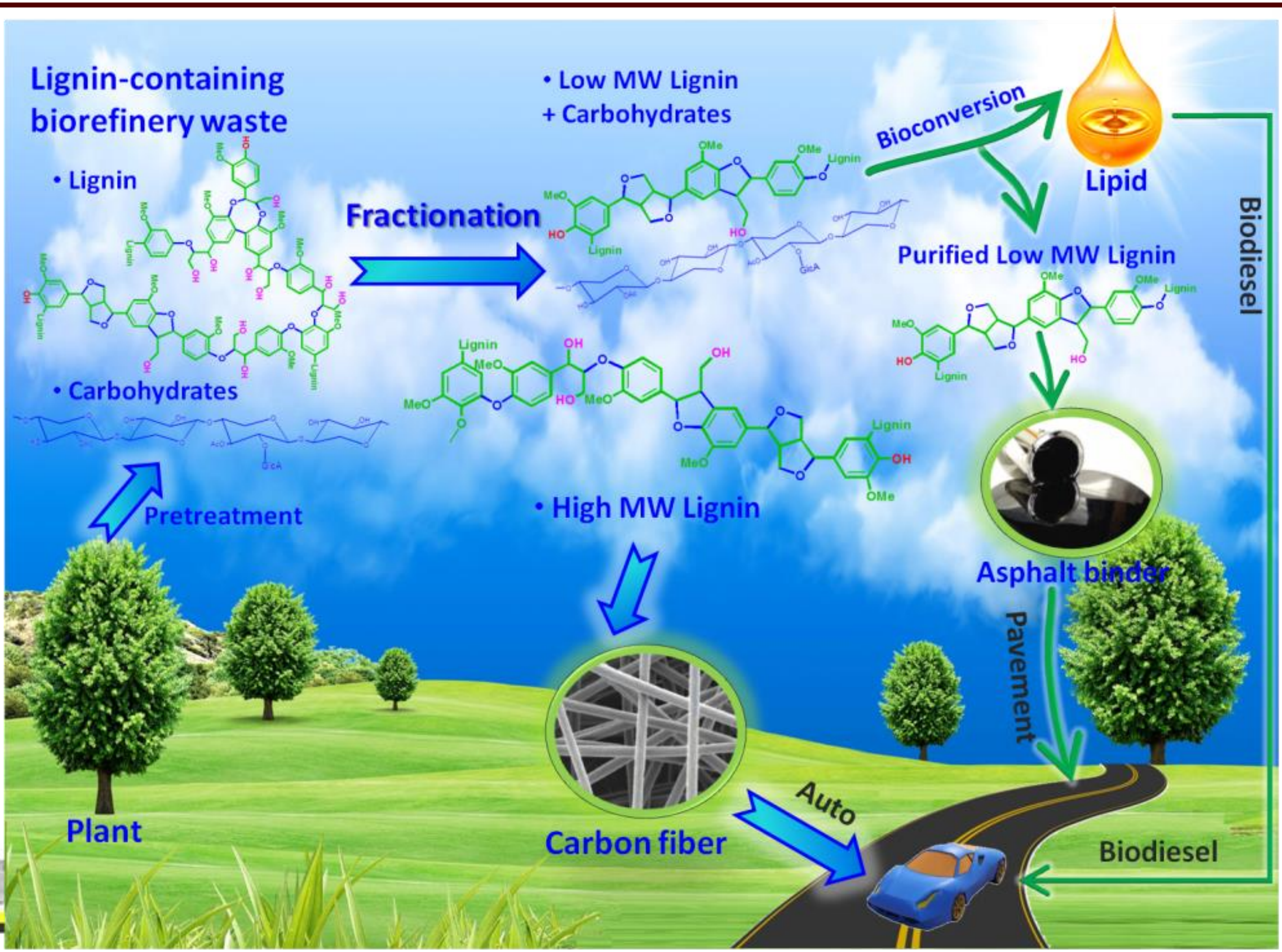
Project Goal: MIBR for Cost-effective and Sustainable Biorefinery

The project will leapfrog the technologies to enable multi-stream integrated biorefinery (MIBR) as measured by a set of complex technical targets including:

- Bioconversion: 60% solubilized biorefinery waste, 25 g/L lipid titer, and 30% conversion rate
- Carbon fiber: 100GPa elastic modulus and 2GPa tensile strength, making lignin fiber ready for commercial utilization
- Asphalt binder modifier: Increasing rutting temp by 10^{o}C
- **Integrating 2 out of the 3 aforementioned products to achieve MESP reduction by $0.5.**

- BETO Missions:
  - Improve biorefinery economics and sustainability
  - Produce high value bioproducts and manage biorefinery waste
  - Reduce carbon emission by complete biomass usage

Project Goal: MIBR for Cost-effective and Sustainable Biorefinery



Key Milestones

- For carbon fiber mechanical performance, **the elastic modulus will be higher than100GPa & the tensile strength will be higher than 2.0 GPa.** Such a mechanical performance will be relevant to commercialization, as the carbon fiber will be ready for composite material for broad applications.
- Lipid titer **25g/L for conversion** of lignin-rich fractionated waste.
- Asphalt binder modifier: improve high temp performance by 10^{o}C.
- At least two out of three streams will be integrated and scaled up at 1DTPD.
- The TEA will show that the integrated process will **reduce biofuel price by $0.5/GGE.**

Key Milestones

Task	Year 1				Year 2				Year 3			
	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Objective 1. MIBR Process Development												
Subtask 1.1, Biorefinery Waste Composition Analysis			*									
Subtask 1.2, Fractionation Technology Development				*					*			
Subtask 1.3, Develop High Quality Lignin-based Carbon Fiber							*					*
Subtask 1.4, Improve Fermentation of Biorefinery Waste								*				
Subtask 1.5, Develop Aromatics-based Asphalt Binder Modifier						*						
Objective 2 MIBR Process Integration and Evaluation												
Subtask 1.1, Process Integration and Design										*		
Subtask 1.2, Technoeconomic Analysis	*											*
Subtask 1.3, Life Cycle Analysis		*									*	
Objective 3. MIBR Scale up												
Subtask 3.1, Scale Up on Site of Biorefinery												*

Project Title:		Multi-stream Integrated Biorefinery (MIBR)					
Task Number	Task Title	Milest. Type	Milest. No.	Milestone Description	Milestone Verification	Mn	Qu
N/A	Program Management Plan		Q1.1	Pass the program management plan	No Validation needed	3	1
1	External Validation	Go/No-Go	Q1.1	Pass the external validation of Appendix G	External third party	3	1
2.1	Biorefinery Waste Composition Analysis		Q3.1	Establish analysis covering 95% of waste composition	Experimental by performer	9	3
2.2	Fractionation Technology Development	Go/No-Go	Q4.1	Fractionation technology to solubilize >40% refinery waste	Experimental by performer	12	4
			Q9.1	Fractionation technology to solubilize >60% refinery waste	Experimental by performer	27	9
2.3	Improve Fermentation of Biorefinery Waste for Lipid	Go/No-Go	Q8.1	Lipid titer 25g/L & Consumption of >80% of carbohydrate	External third party	24	8
2.4	Develop Aromatics-based Asphalt Binder Modifier		Q6.1	Improve high temp performance by $10^{o}C$	Experimental by performer	18	6
2.5	Develop High Quality Lignin-based Carbon Fiber		Q7.1	50GPa on modulus & 1.0GPa tensile strength	Experimental by performer	21	7
		Go/No-Go	Q12.1	100GPa modulus & 2.0 GPa tensile strength	Experimental by performer	36	12
3.2	Technoeconomic Analysis		Q1.2	Establish a TEA model to integrate all 3 product streams	Submit to DOE	3	1
		Go/No-Go	Q12.2	Reduce MESP by $2/GGE	Submit to DOE	36	12
3.3	Life Cycle Analysis		Q2.1	Establish a Greet Model to integrate all product streams	Submit to DOE	6	2
			Q11.1	Reduce carbon emission of biorefinery by 10%	Submit to DOE	33	11
4.1	Scale up on site of biorefinery	Go/No-Go	Q12.3	25g/L lipid titer at 1 DTPD (>100Kg solubilized waste), 60% carbon yield for carbon fiber	External third party	36	12

Quad Chart Overview

Timeline

- Project start date: 09/01/2018
- Project end date: 08/31/2021
- Percent complete: 5%

Budget

	Total Costs Pre FY17**	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	$0	$0	$68,156	$1,481,088
Project Cost Share*	$0	$0	$16,929	$842,127

Barriers

- Barriers addressed
  - Ot-B. Cost of Production
  - Ct-B. Efficient Preprocessing and Pretreatment
  - Ct-C. Process Development for Conversion of Lignin
  - Ct-D. Advanced Bioprocess Development
  - Ct-J. Identification and Evaluation of Potential Bioproducts
  - Ct-K. Developing Methods for Bioproduct Production
  - Ct-L. Decreasing Development Time for Industrially Relevant Micro organisms
  - ADO-A. Process Integration
  - ADO-D. Technology Uncertainty of Integration and Scaling
  - At-D. Identifying New Market Opportunities for Bioenergy and Biop roducts
  - At-E. Quantification of Economic, Environmental, and Other Benefi ts and Costs

Partners

- Partners
  - University of Tennessee, Knoxville/ Oak Ridge National Laboratory
  - Washington State University
  - ICM inc.
- Commercial Partners and Relevance
  - ICM inc. to scale up the technology to 1 Dry ton per day in an integrated biorefinery.

Project Overview

FOA Topic: Topic Area 2: High value products from waste/or other undervalued streams in an integrated biorefinery.

Project Title:

Multi-stream Integrated Biorefinery Enabled by Waste Processing

Objectives:

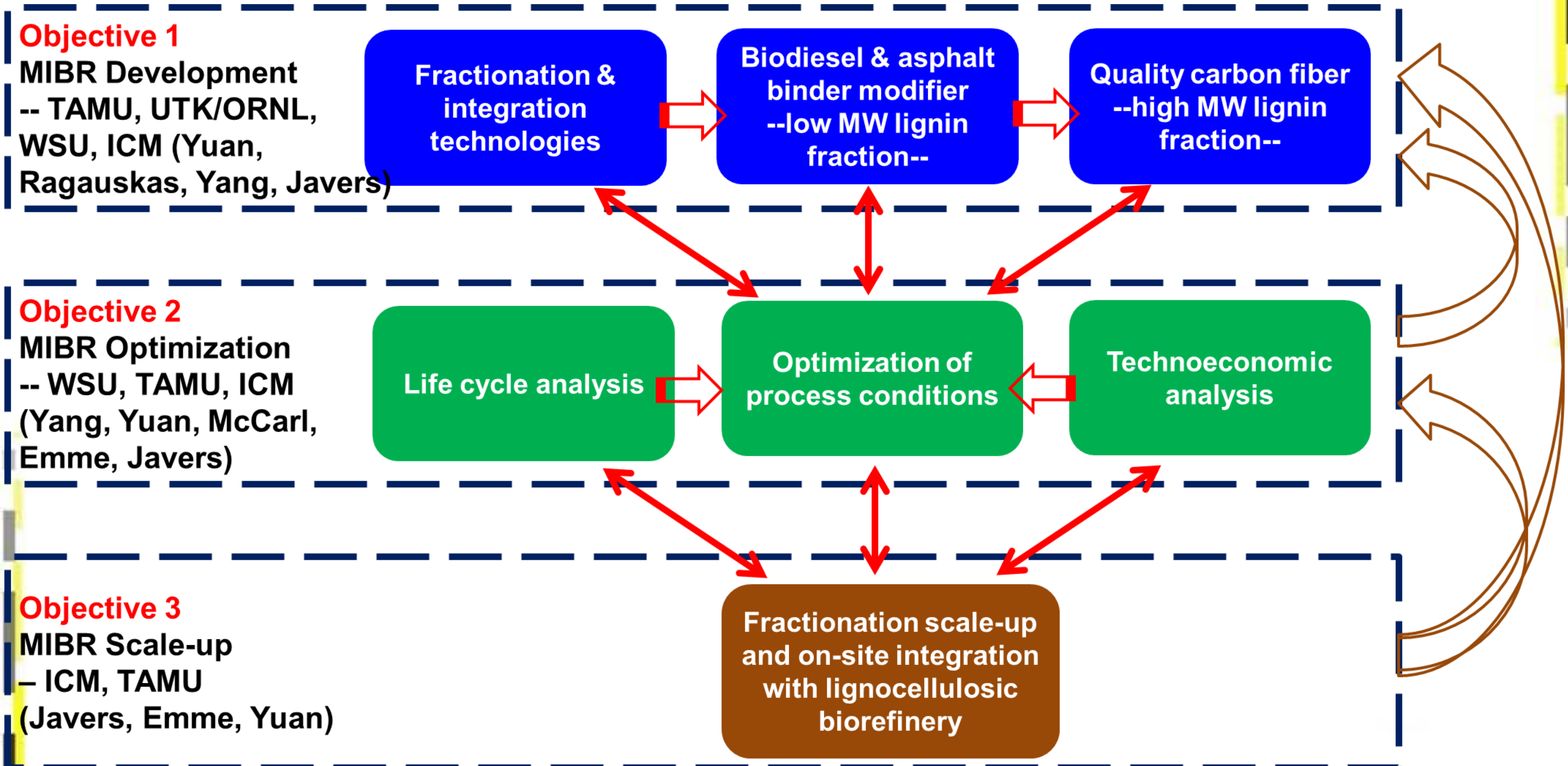
The project will integrate recent advances developed by a multidisciplinary academic-industrial coalition to address one of the most challenging issues in lignocellulosic biofuel: the utilization of biorefinery waste in producing valuable products. The success of a modern biorefinery heavily depends on the creation of diverse and valuable product streams using all fractions of input material.

- Objective 1. MIBR development by advancing fractionation, conversion, and processing technologies to enable valuable bioproduct streams.
- Objective 2. MIBR optimization through process design, technoeconomic analysis (TEA), and life cycle analysis (LCA).
- Objective 3. MIBR scale-up to 1DTPD (dry ton per day) capacity.

Management Approach

- Defined and measurable milestones were laid out for technology development and commercialization.
- Go/No-Go milestones were set at the end of each year and each of the three budget periods. BP1 ends at month 6, and BP2 ends at month 24.
- Monthly group teleconferences and teleconference with program management were implemented to evaluate the progresses against milestones.
- Regular teleconferences between the PI and the program management are implemented to evaluate progresses, mitigate risks, and address management issues.
- Engage industrial partners including ICM inc. for deliverables relevant to EERE MYPP.
- Integrate TEA and LCA throughout the project to ensure the relevance of the project outcome.

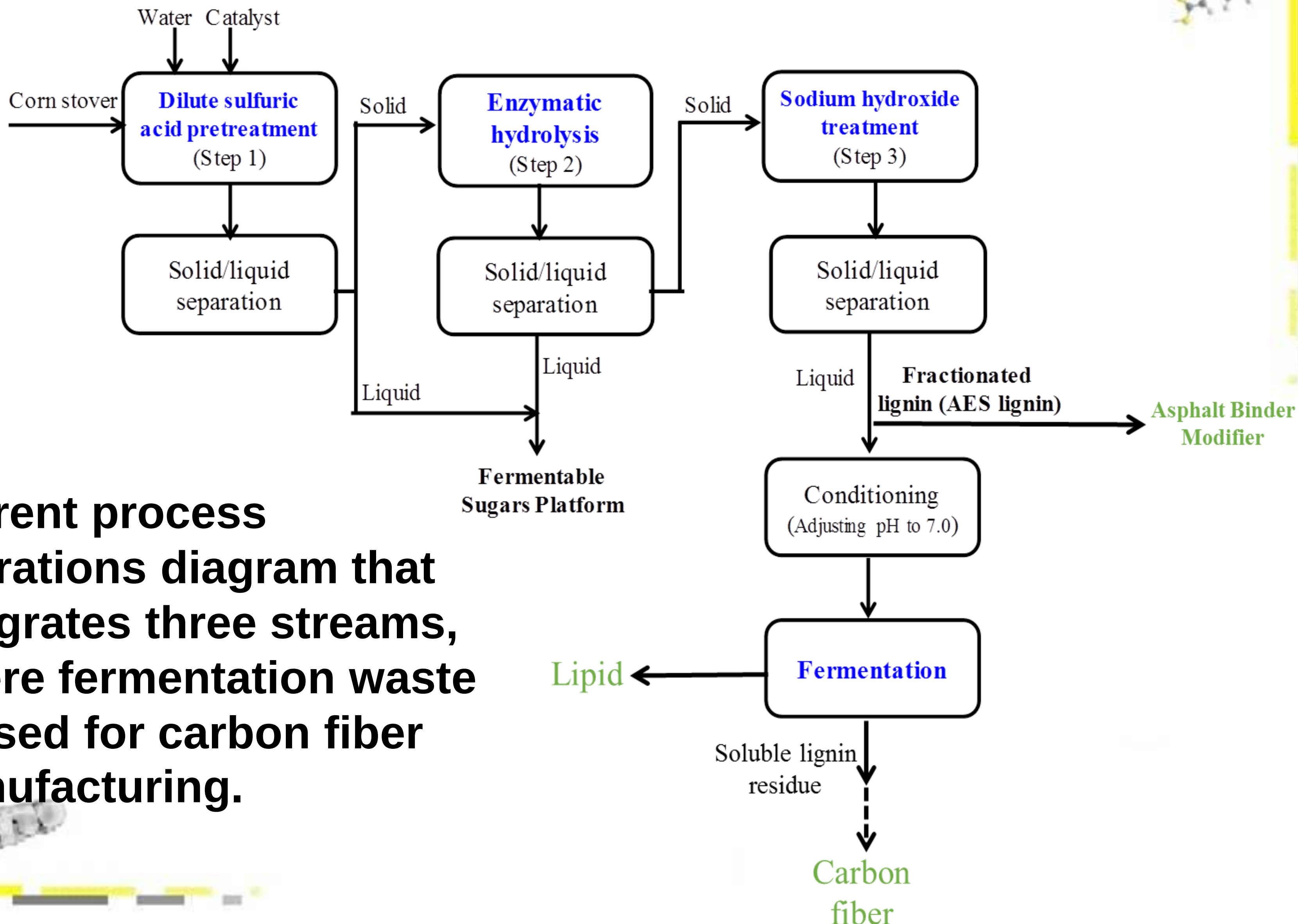
Technical Approach



Technical Approach

- MIBR Development:
  - Pretreatment and fractionation technologies to enable three streams
  - Lignin to lipid conversion process development and optimization
  - Lignin to asphalt binder modifier development
  - Lignin to carbon fiber process development and optimization
- MIBR Optimization and integration
  - Optimization and integration of three processes
  - Technoeconomic analysis to guide the optimization and integration
  - Life cycle analysis to evaluate the process
- MIBR Scale-up
  - The scale up to 1DTPD scale

Approach – Process Operations Block Diagram



Current process operations diagram that integrates three streams, where fermentation waste is used for carbon fiber manufacturing.

Technical Achievement

- Understand the relationship between lignin chemistry and carbon fiber performance.
- Achieved >40GPa Elastic Modulus and >300MPa tensile strength on lignin carbon fiber
- Achieved >10g/L lipid titer.
- Achieved >7^{o}C improvement of high temperature performance for asphalt binder modifier.
- Lay down the foundation for TEA integration of all streams

Relevance – Direct Relevance to MYPP and Challenges in Biorefinery

- The project will convert biorefinery residues to 2-3 biorefinery streams, which will enable MIBR. The project provides multiple value-added products for biorefinery to improve economics, avoid market saturation, and achieve sustainability.

- The project will enable the multi-stream integrated biorefinery (MIBR) to maximize the yield of both carbohydrate-based biofuels and lignin-based bioproducts, which will turn biorefinery into biomanufacturing facility.

- With the multiple product stream and the maximized yield for both biofuels and bioproducts, the project well address the MYPP goal to achieve $3/GGE fuels. The project will improve the overall cost-effectiveness of biorefinery and reduce MESP by $0.5.

- With more complete utilization of biorefinery residues, the project will address the mission of BETO, the MYPP goals, and the challenges in biofuel industry by improving biorefinery efficiency and sustainability.

- The research has a significant potential to reduce MESP.

Relevance – Lignin Utilization to Enable Multistream Biorefinery

Cellulosic Biomass

Lignin Waste

Lignin Conversion

Additional Bioproducts and Biofuel Streams

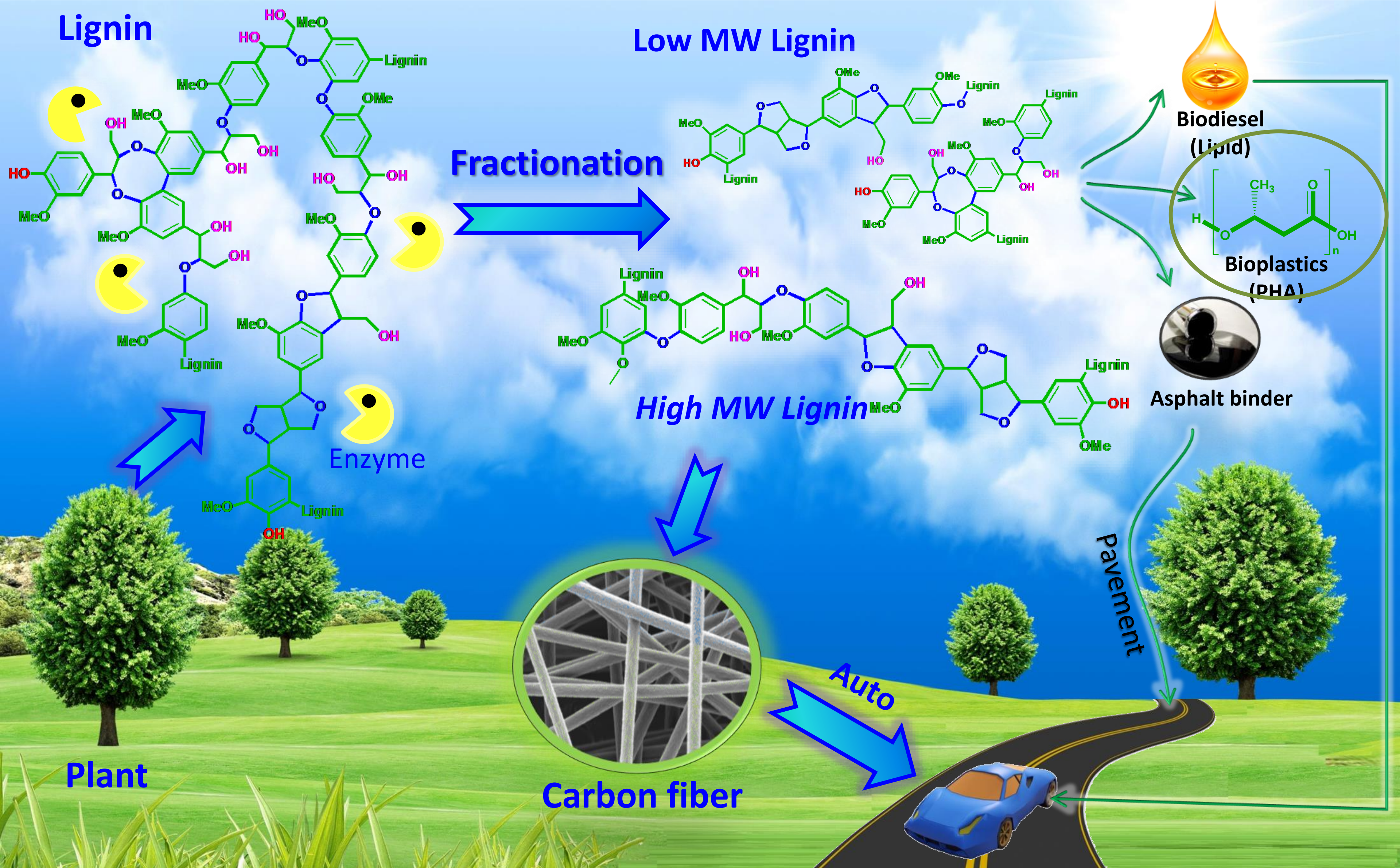
Carbohydrate Conversion

- Pretreatment
- Hydrolysis
- Fermentation

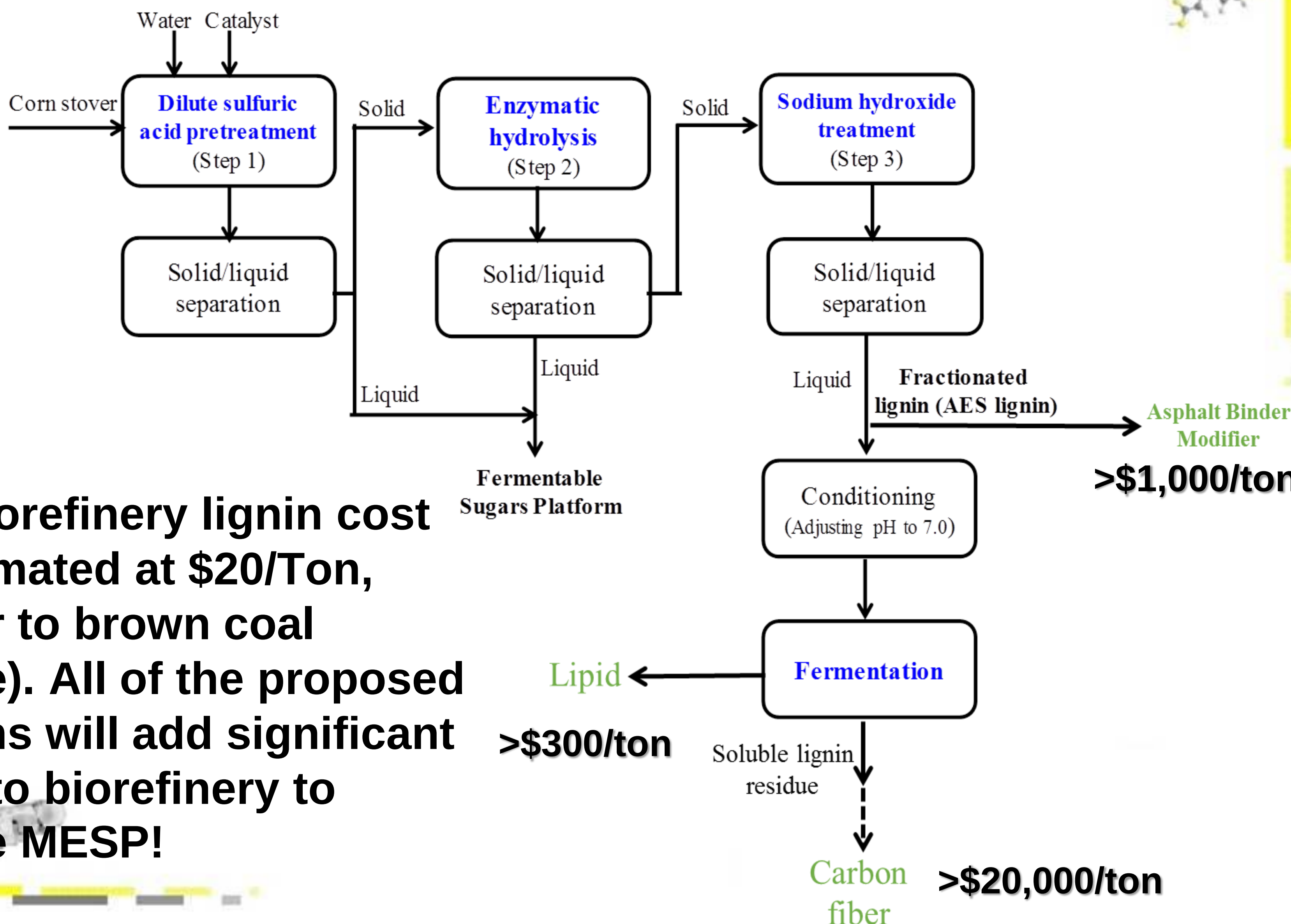
Fuel finishing and blending

Xie, et al. Industrial Biotechnology 12 (3), 161-167

Relevance – Enabled Multistream Integrated Biorefinery (MIBR)



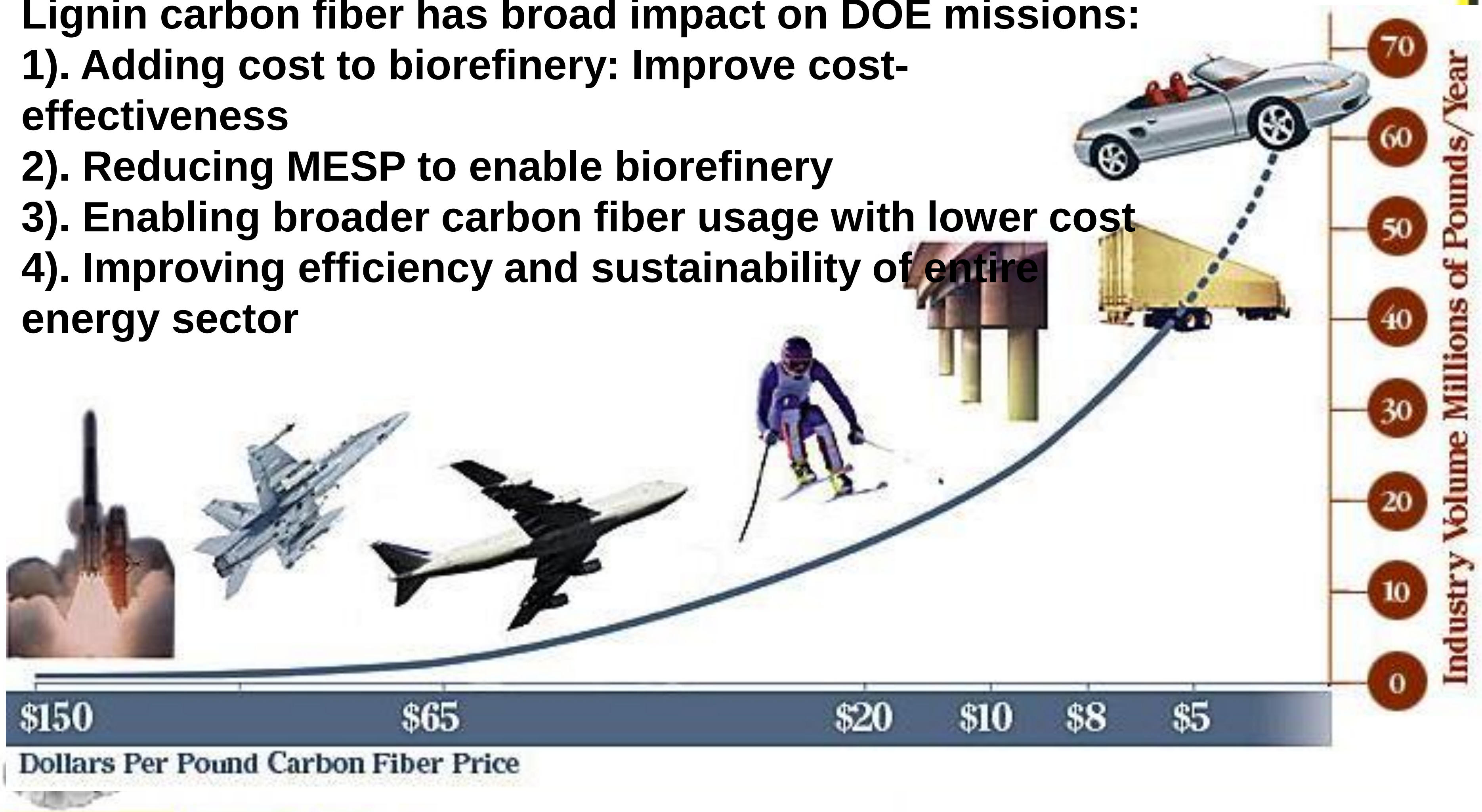
Relevance – Multiple Value-adding Products



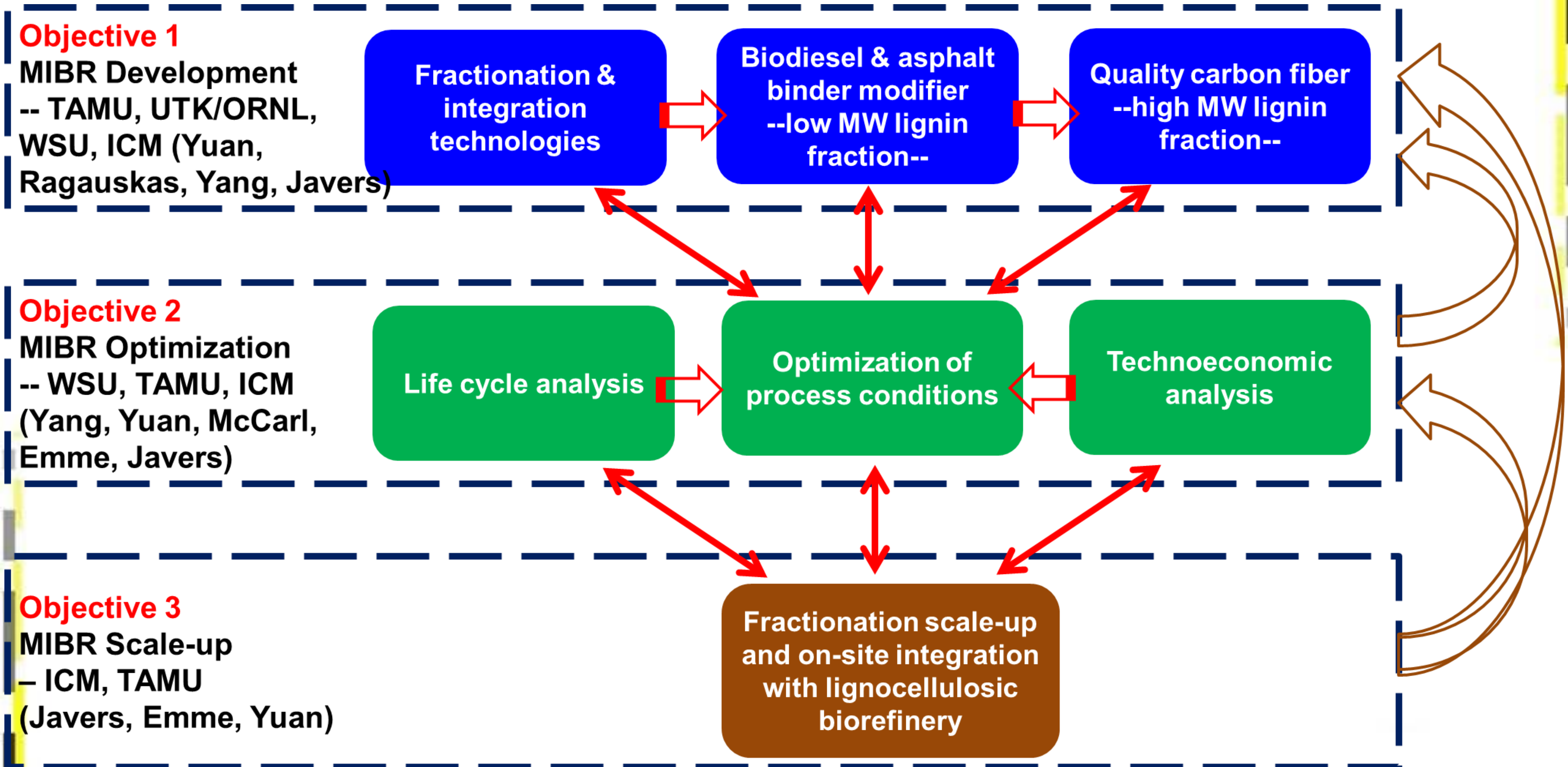
The biorefinery lignin cost is estimated at $20/Ton, similar to brown coal (lignite). All of the proposed streams will add significant value to biorefinery to reduce MESP!

Relevance – Lignin as a Promising Substitute for Carbon Fiber Precursor

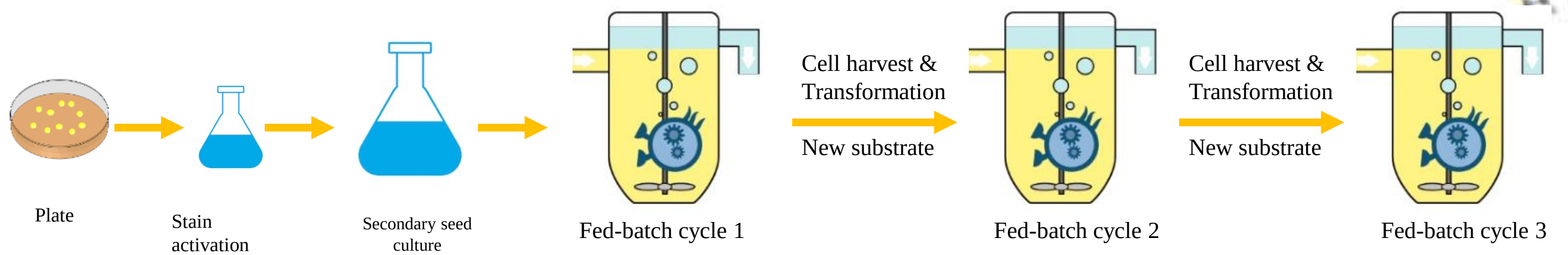
Lignin carbon fiber has broad impact on DOE missions:
1). Adding cost to biorefinery: Improve cost-effectiveness
2). Reducing MESP to enable biorefinery
3). Enabling broader carbon fiber usage with lower cost
4). Improving efficiency and sustainability of entire energy sector



Future Work


Objective 1
MIBR Development
-- TAMU, UTK/ORNL, WSU, ICM (Yuan, Ragauskas, Yang, Javers)
Fractionation & integration technologies
Biodiesel & asphalt binder modifier --low MW lignin fraction--
Quality carbon fiber --high MW lignin fraction--
Objective 2
MIBR Optimization
-- WSU, TAMU, ICM (Yang, Yuan, McCarl, Emme, Javers)
Life cycle analysis
Optimization of process conditions
Technoeconomic analysis
Objective 3
MIBR Scale-up
– ICM, TAMU (Javers, Emme, Yuan)
Fractionation scale-up and on-site integration with lignocellulosic biorefinery

Future Work – Lipid Stream



- EG *R. opacus PD630*
- AES LIGNIN
- **40 g/l SSC**
- 1.4 g/l NH_4Cl
- 1 L
- 72 hours
- pH 7.0
- 30 °C
- 400 rpm

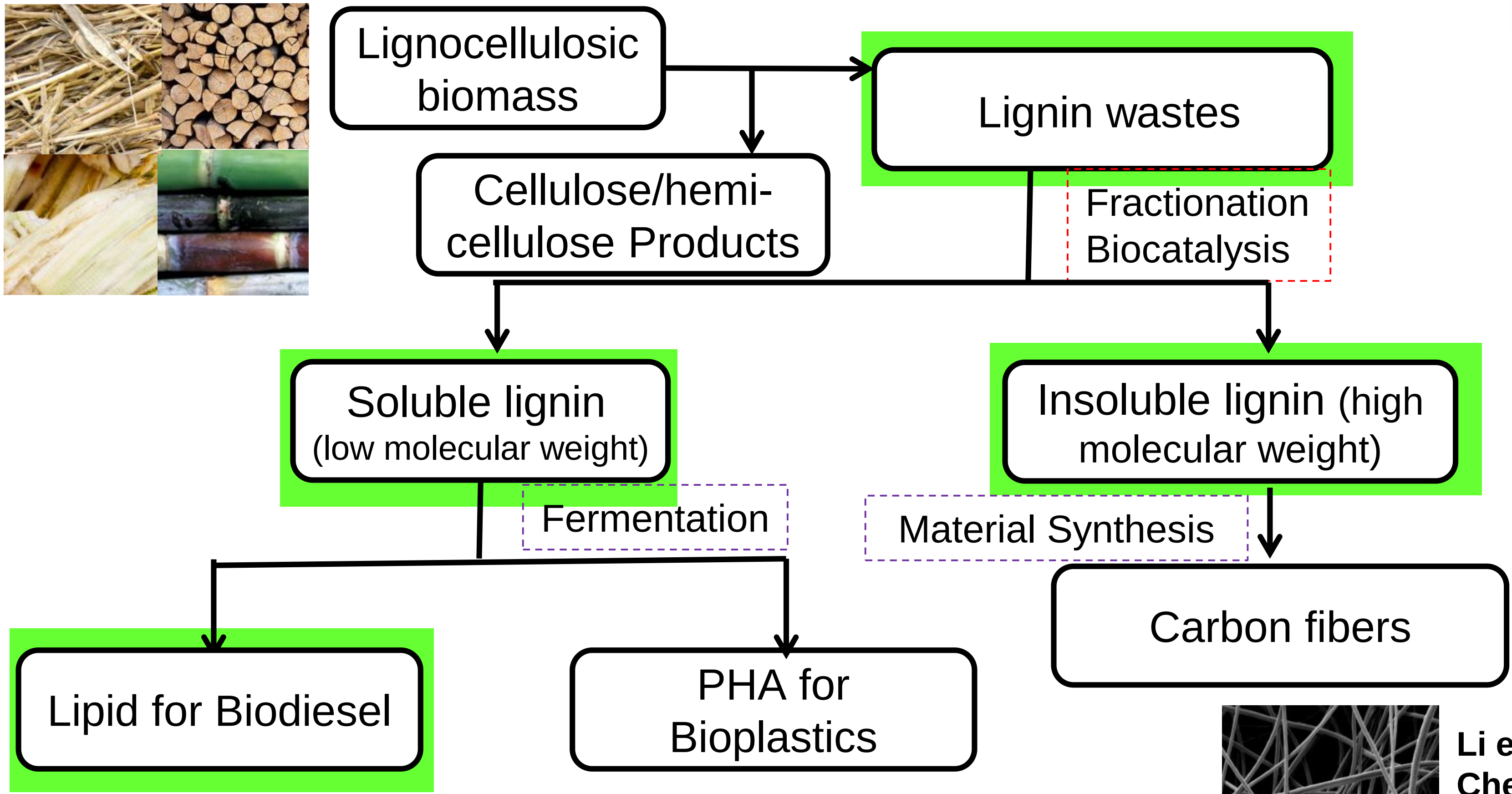
- EG *R. opacus PD630*
- AES LIGNIN
- 40 g/l SSC
- 1.4 g/l NH_4Cl
- 1 L
- 72 hours
- pH 7.0
- 30 °C
- 400 rpm

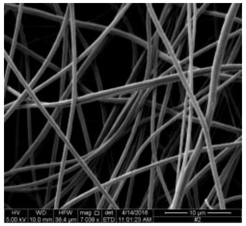
- EG *R. opacus PD630*
- AES LIGNIN
- 40 g/l SSC
- 0 g/l NH_4Cl
- 1 L
- 72 hours
- pH 7.0
- 30 °C
- 400 rpm

	SSC/g/l	Fed batch cycle	Fermentation time	Cell dry weight / g/l	Lipid yield (g/l)	DE-foaming	Control oxygen
Flask	40	3	7 days	27.6	10.09	-	-
Fermentor	40	3	7 days	19.52	8.73	Yes	-
Fermentor	40	3	7 days	32.99	10.52	Yes	Yes

We will continue to engineer R. opacus strain, optimize the fermentation conditions, and improve fractionation technologies. Some strategies already improved lipid yield.

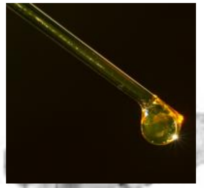
Future Work: Lignin to Carbon Fiber





Li et al., Green Chemistry, 2017, 19, 1628-1634

Li et al., J. Materials Chemistry A, 2017, 5, 12740-12746
Li et al., TAPPI J. 2017, 16, 107-108

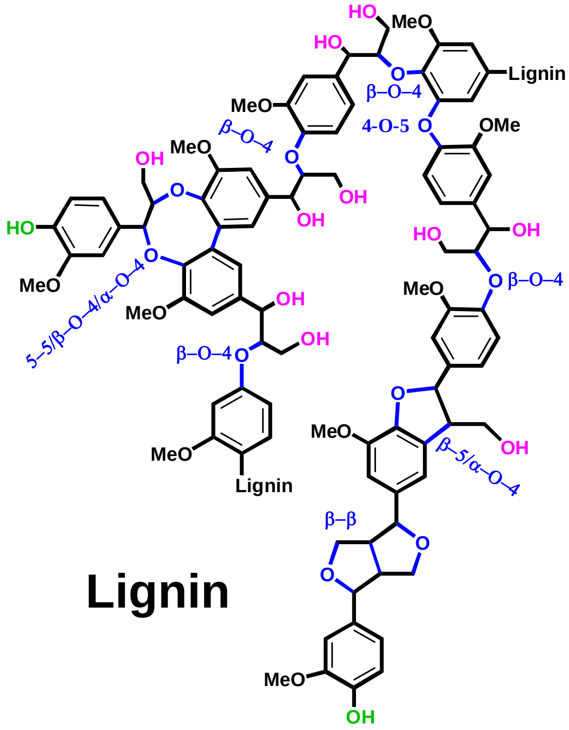


Zhao et al., Green Chemistry, 2016, 18, 2802-2810.
Xie et al., ACS Sustainable Chemistry & Engineering, 2017, 5, 2215-2223

Lin, et al., Green Chemistry, 2016, 18, 5536-5547.
Liu, et al., Green Chemistry, 2017, 19, 4939-4955

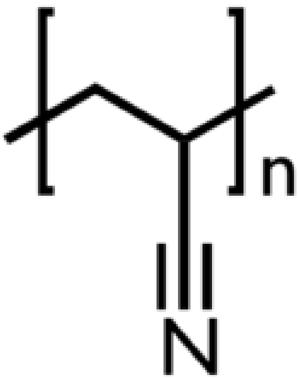
Challenges of Lignin Carbon Fiber

Lignin Carbon Fiber



Lignin

PAN Carbon Fiber



Polyacrylonitrile

Homogeneous polymer

Comparable

- *Spinnability*
- *Miscibility*
- *Performance*

Heterogeneous:

--Interunitery linkages

--Functional groups

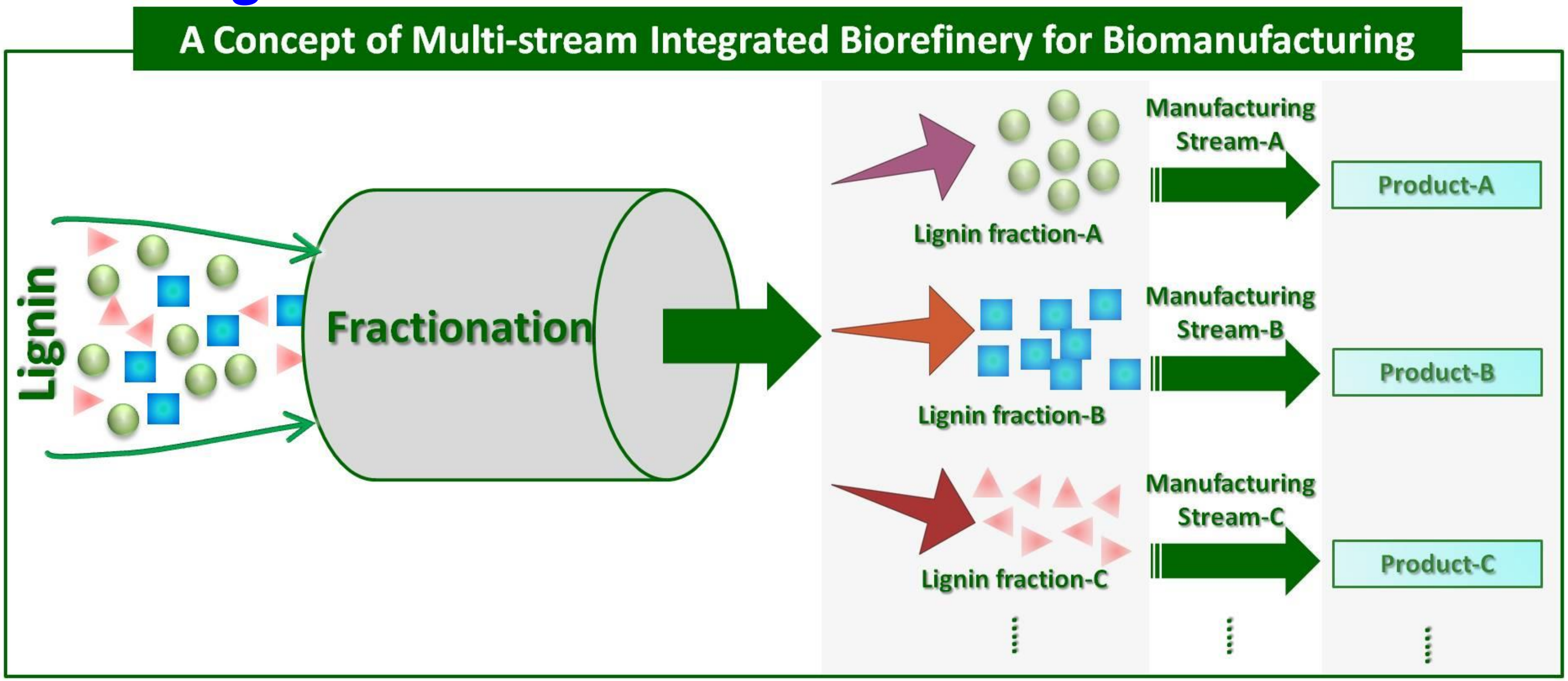
--Molecular weight

Scientific Hypothesis for Quality Lignin Carbon Fiber

Lignin heterogeneity ⟷ ✗ ***Carbon fiber***

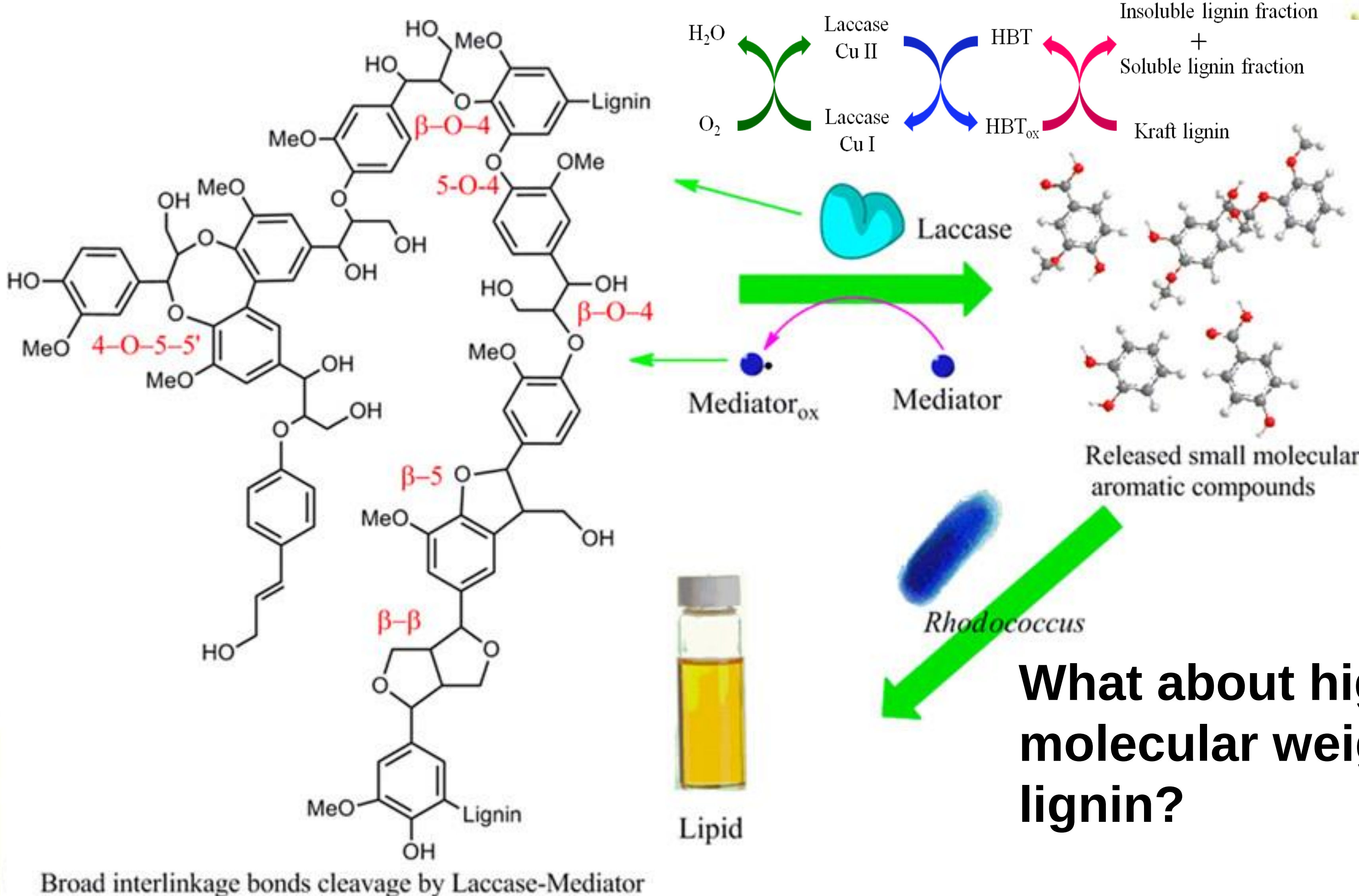
Hypothesis:

Fractionation can produce less heterogeneous/more uniform lignin fractions



Li et al. Lignin Carbon Fiber: the Path for Quality. Tappi J. 2017, 16, 107-108.

Lignin Fractionation by Laccase-Mediator system



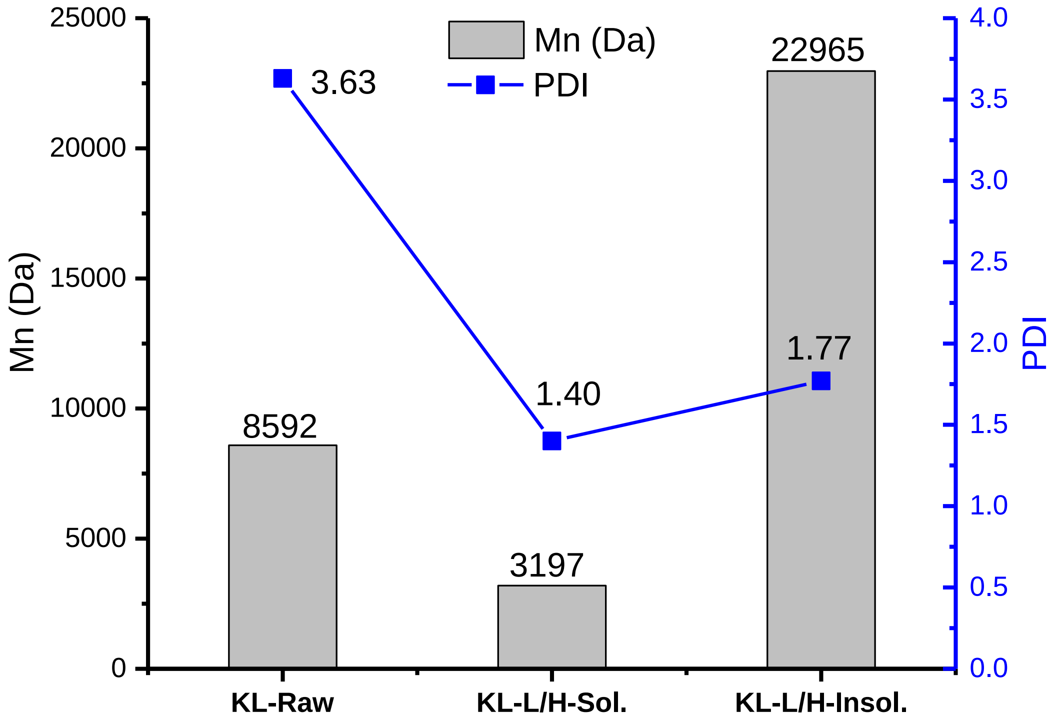
What about high molecular weight lignin?

Xie, et al., ACS Sustain. Chem. Eng. 2017, 5, 2215-2223

Characterization of Fractionated Lignin

1) Molecular weight

(Size Exclusion Chromatography, SEC)



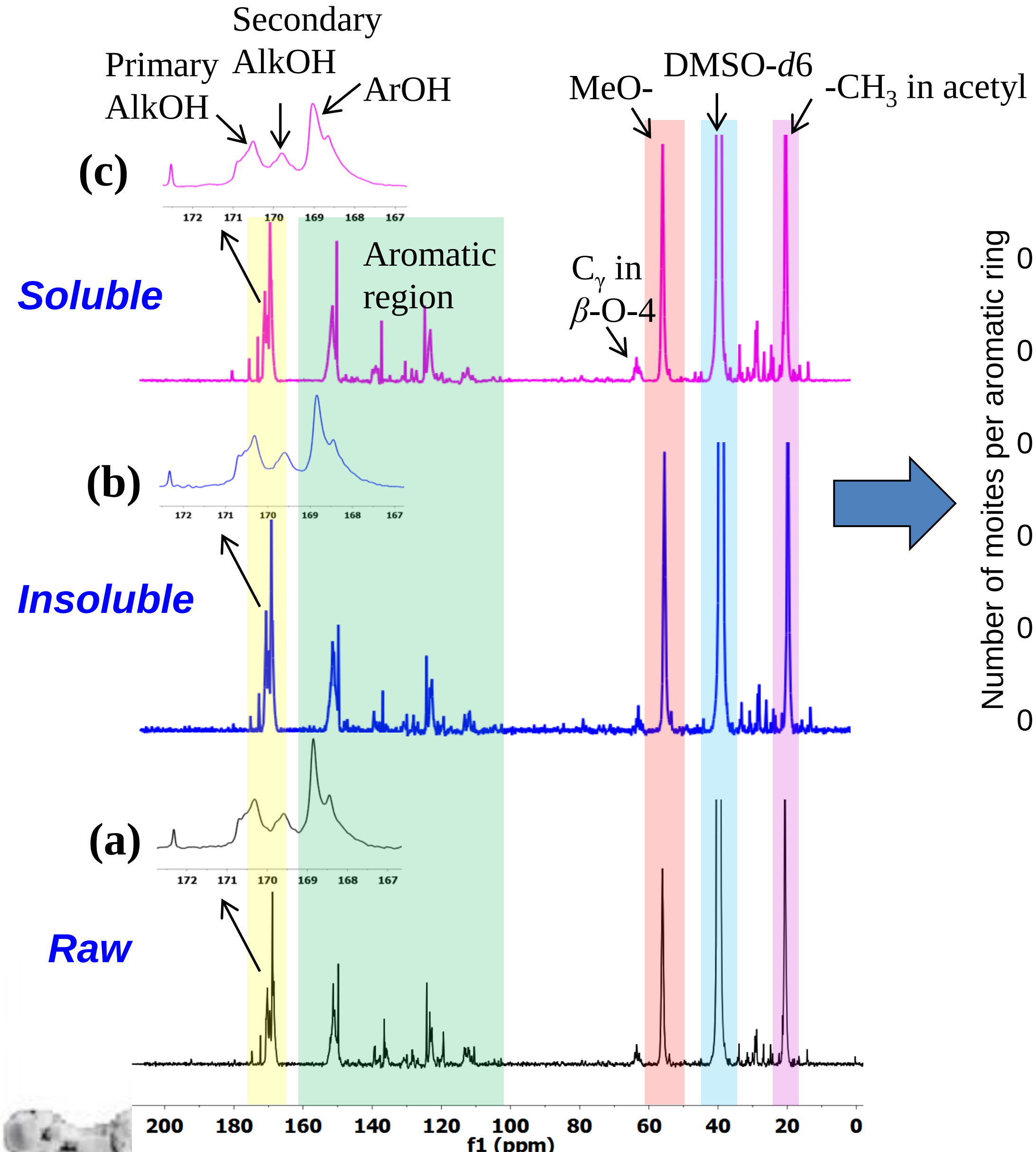
System: OMNISEC system (Malvern Instrument Ltd., Houston, TX).
Column: Two D6000 + one Viscotek D-Columns
Eluent: Tetrahydrofuran (THF);
Detertor: RI, UV (280 nm), viscometer
Column temperature: 45 °C;
Flow rate: 1.0 mL/min;
Injection volume: 100 μL
Internal standard: polystyrenes;
Universal calibration

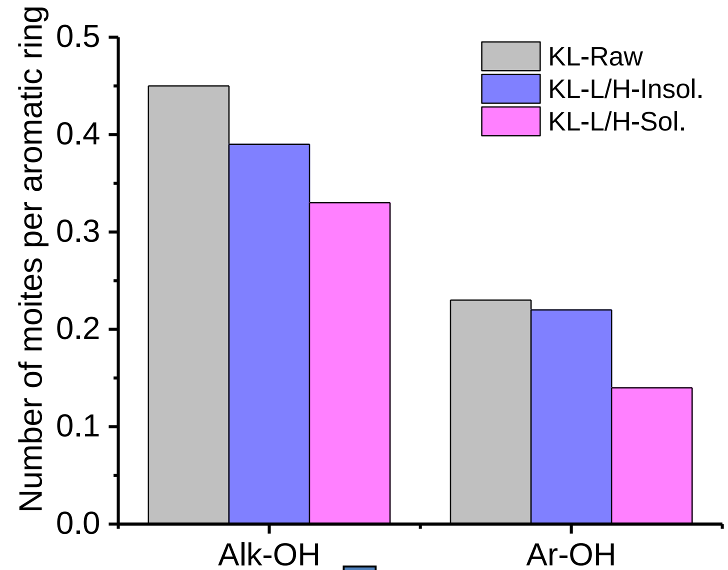
PDI: polydispersity index

Soluble: MW & PDI ↓ **Insoluble: MW ↑ , PDI ↓**

Li, et al., *Green Chemistry*, 2017, 19, 1628-1634.

Hydroxyl Groups (-OH) by ^{13}C NMR



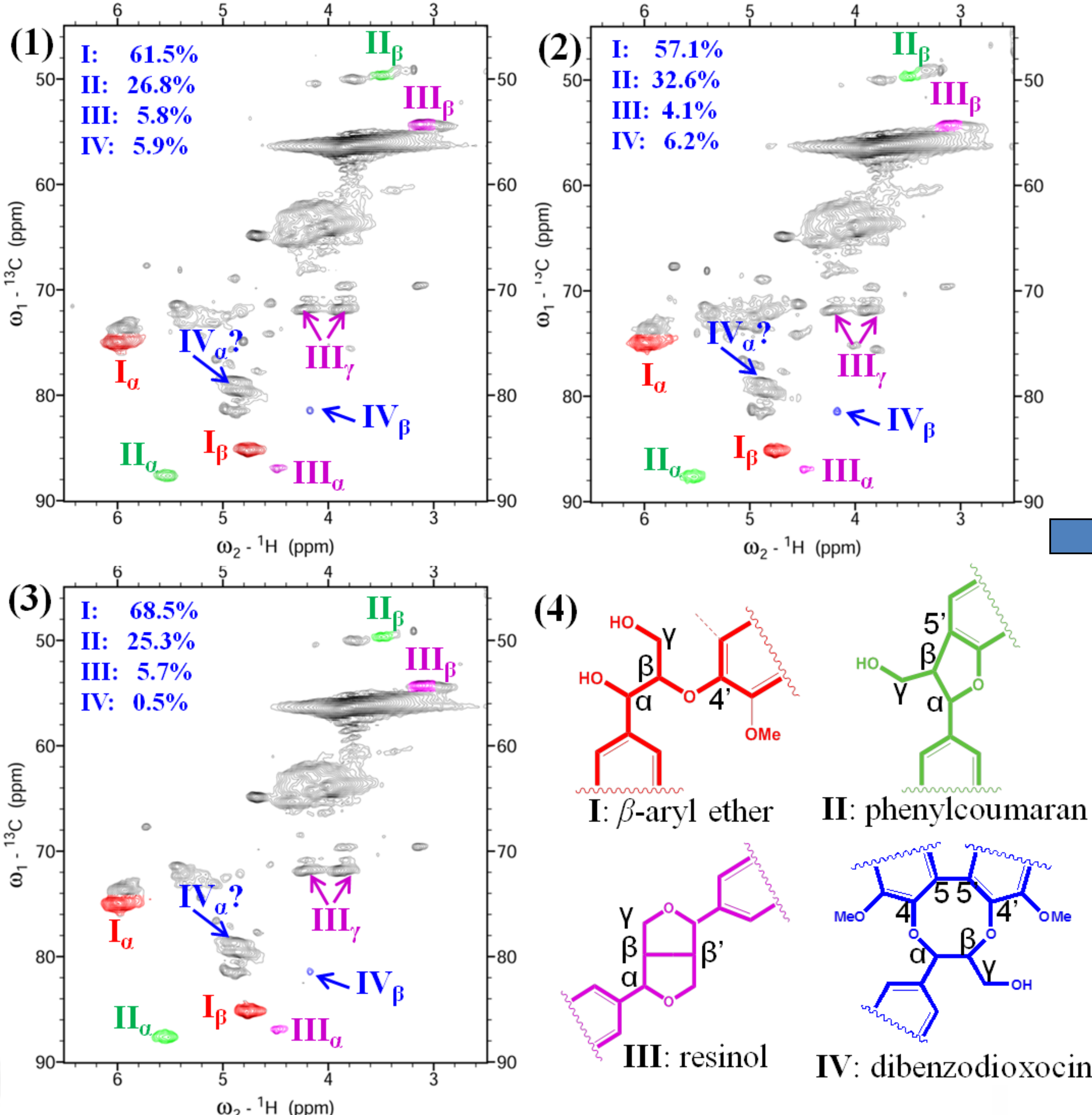


Soluble & Insoluble: -OH

Alk-OH: aliphatic -OH
Ar-OH: phenolic -OH

Li, et al., *Green Chemistry*, 2017, 19, 1628-1634.

Interunitery Linkages by 2D NMR (HSQC)



(1), Raw; (2), Sol.; (3), Insol.

Insoluble fraction:

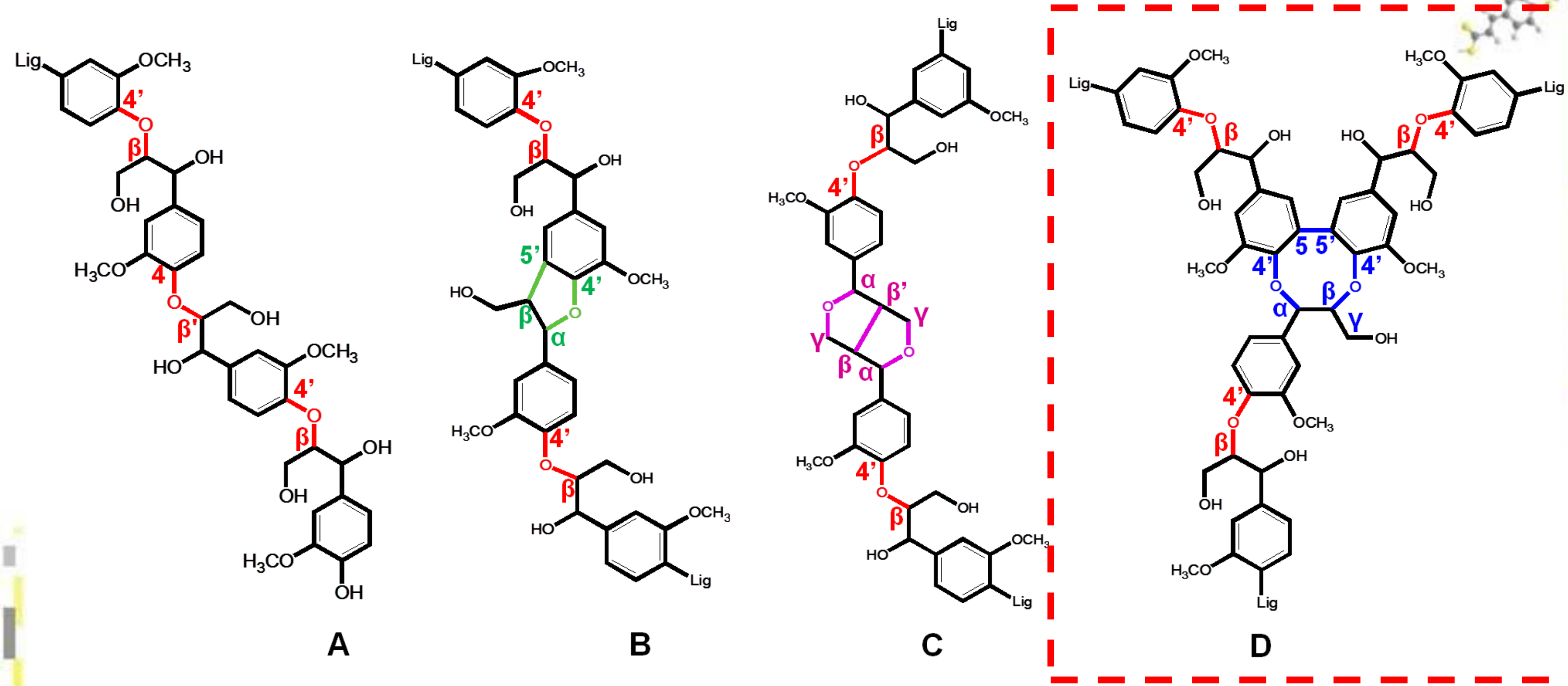
β-O-4: ↑
β-5: ↓
β-β: ----
DBDO: ↓

Soluble fraction:

β-O-4: ↓
β-5: ↑
β-β: ↓
DBDO: ↑

Li, et al., *Green Chemistry*, 2017, 19, 1628-1634.

Interunitery Linkage Type



DBDO: Brach point of lignin

Insoluble fraction:

Decreased DBDO + Increased β-O-4

→More linear

Soluble fraction:

More DBDO + Decreased β-O-4

→Less linear

Li, et al., *Green Chemistry*, 2017, 19, 1628-1634.

Summary of Lignin Fractionation

Fractionated Lignin – An Important Strategy for Future Work:

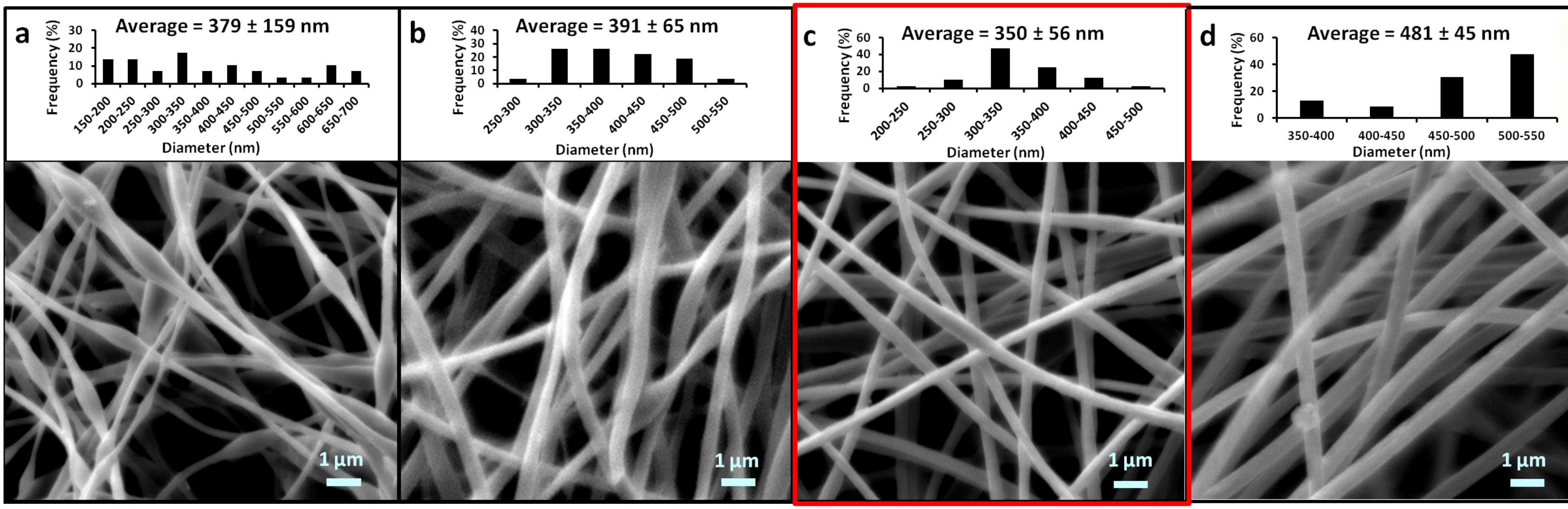
1, Water-insoluble lignin fraction:
Higher molecular weight,
Lower hydroxyl groups,
More linear structure

2, Water-soluble lignin fraction:
Lower molecular weight,
Lower hydroxyl groups,
Less linear structure

Li, et al., *Green Chemistry*, 2017, 19, 1628-1634.

Carbon Fiber from High MW Lignin Has Better Spinnibility

KL-Raw | KL-L/H-Sol. | **KL-L/H-Insol.** | Pure PAN



Li et al. Quality carbon fibers from fractionated lignin. Green Chemistry. 2017, 19, 1628–1634.

Insoluble lignin fraction:

--'Beads' defects free

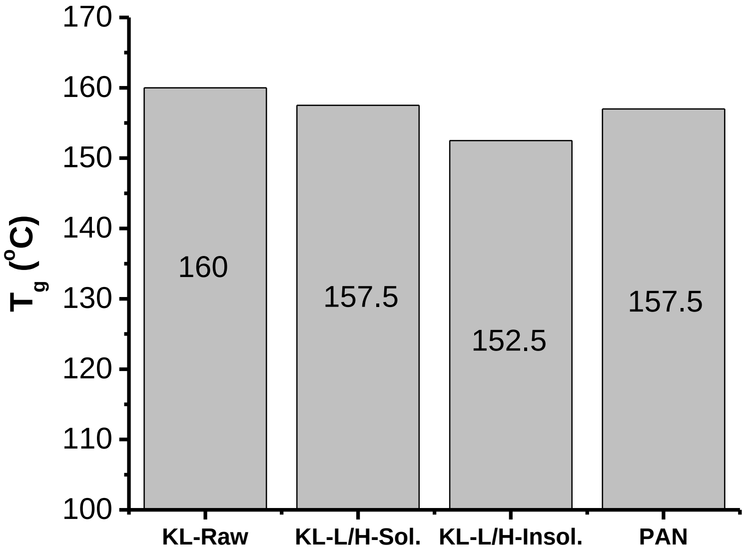
--Smallest diameter

--Uniform diameter distribution

Li, et al., *Green Chemistry*, 2017, 19, 1628-1634.

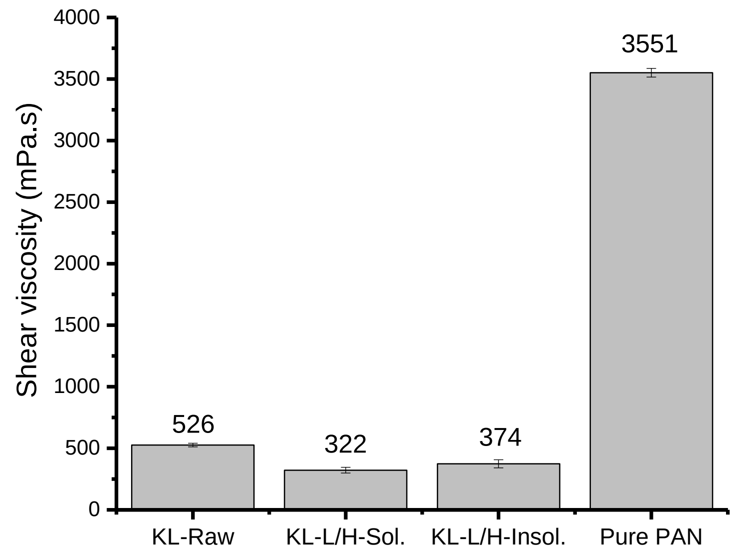
Insoluble Lignin Fraction Has Better Miscibility

Differential scanning calorimetry (DSC)



Glass transition temperature (T_g)

Dynamic viscosity measured by a rotational rheometer



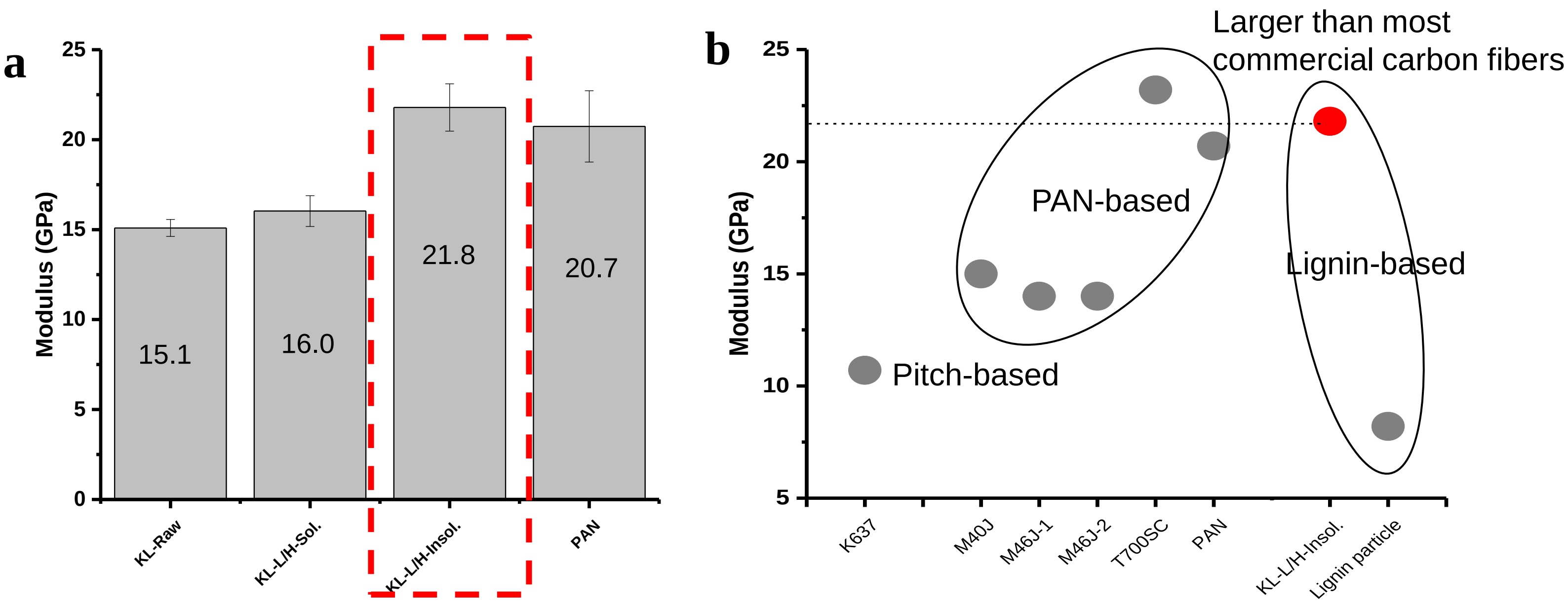
Viscosity

Insoluble lignin fraction:

better miscibility with PAN, lower viscosity

Li, et al., *Green Chemistry*, 2017, 19, 1628-1634.

Lignin Carbon Fiber Has Elastic Modulus Comparable with PAN-based Carbon Fiber

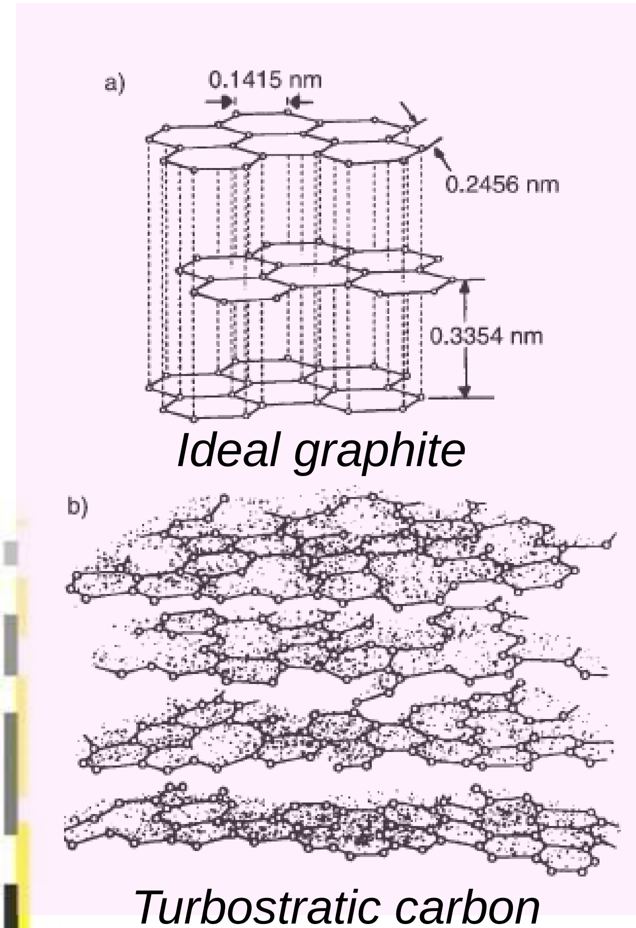


Why so good??

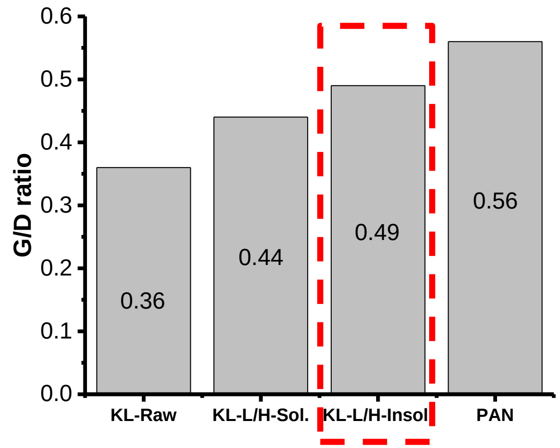
---Crystallite structure

Li, et al., *Green Chemistry*, 2017, 19, 1628-1634.

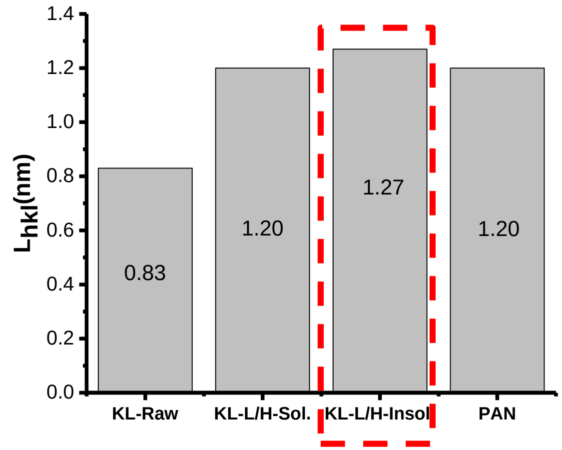
Mechanisms: Pre-graphite turbostratic carbon



Raman spectroscopy (Crystallite content)



XRD (Crystallite size)



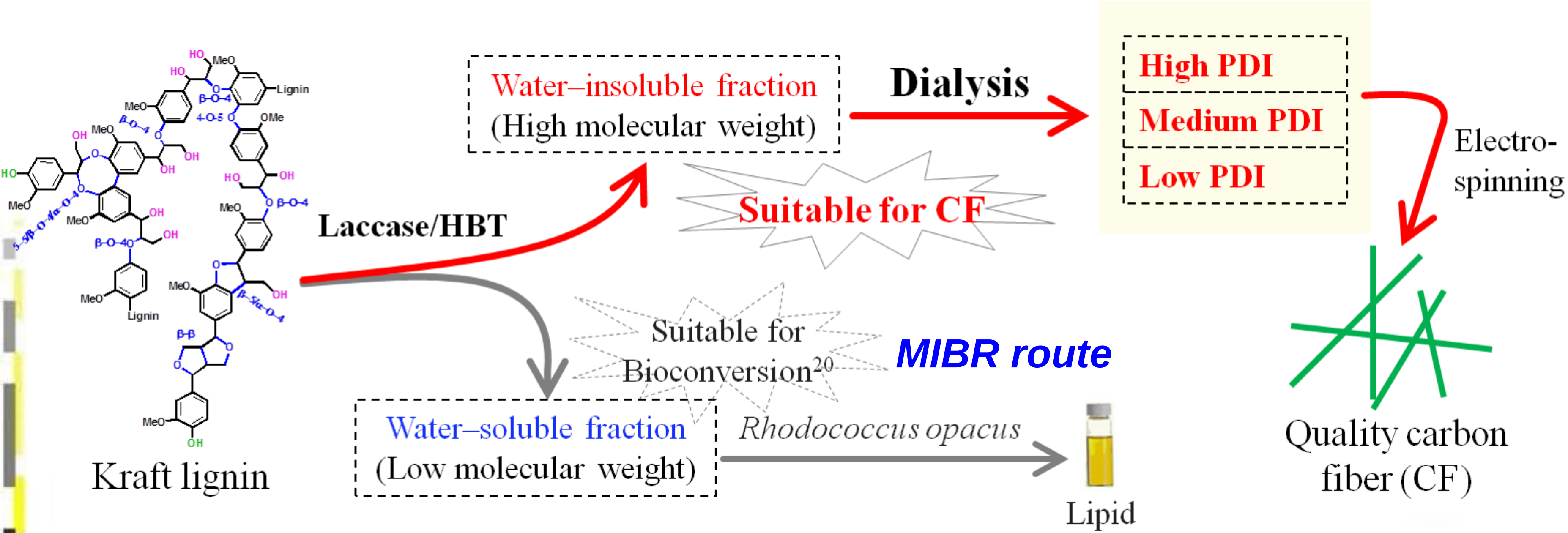
Carbon fiber from insoluble lignin:

Higher G/D ratio, higher crystallite size

Li, et al., *Green Chemistry*, 2017, 19, 1628-1634.

What is Exactly Impacting the Mechanical Performance – More Fractionation

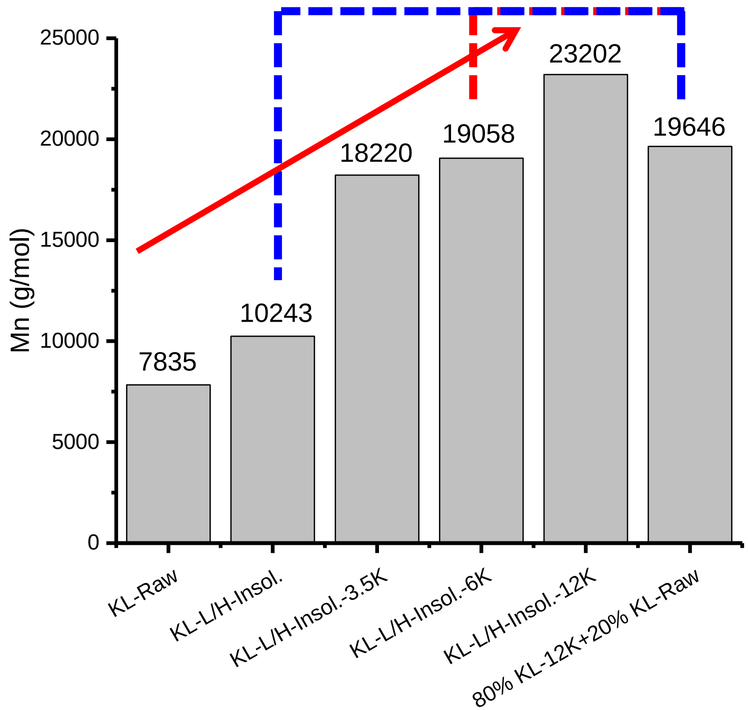
Molecular weight ***or*** **Molecular uniformity (Polydispersity index, PDI) ??**



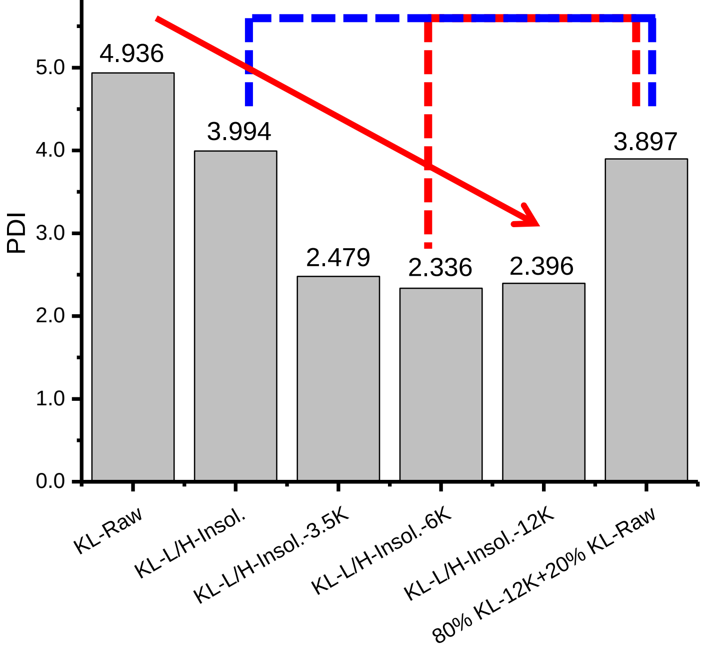
Li, et al., *J. Materials Chemistry A. 2017*. 5, 12740-12746

Diverse Lignin Structure out of Size Exclusion Chromatography, SEC

Molecular weight (Mn)



Polydispersity index (PDI)



MW: KL-Raw **<** KL-L/H-Insol. **<** 3.5K **<** 6K **<** 12K;

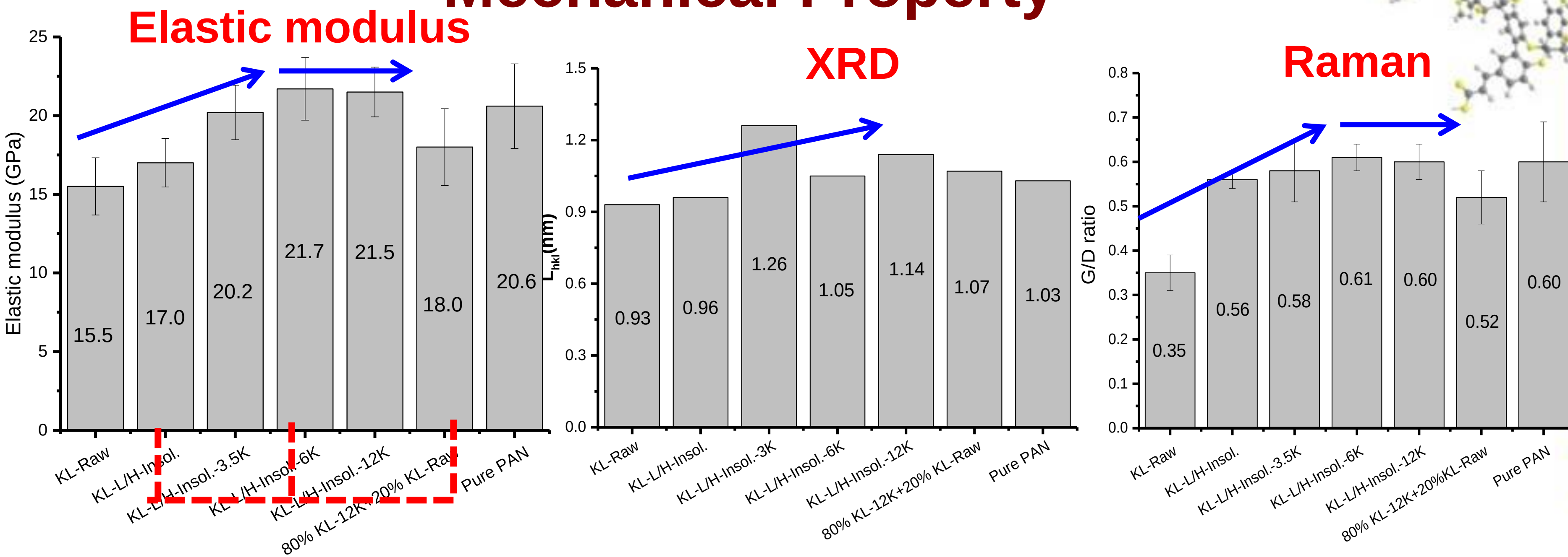
PDI: KL-Raw **<** KL-L/H-Insol. **<** 3.5K **<** 6K **=** 12K;

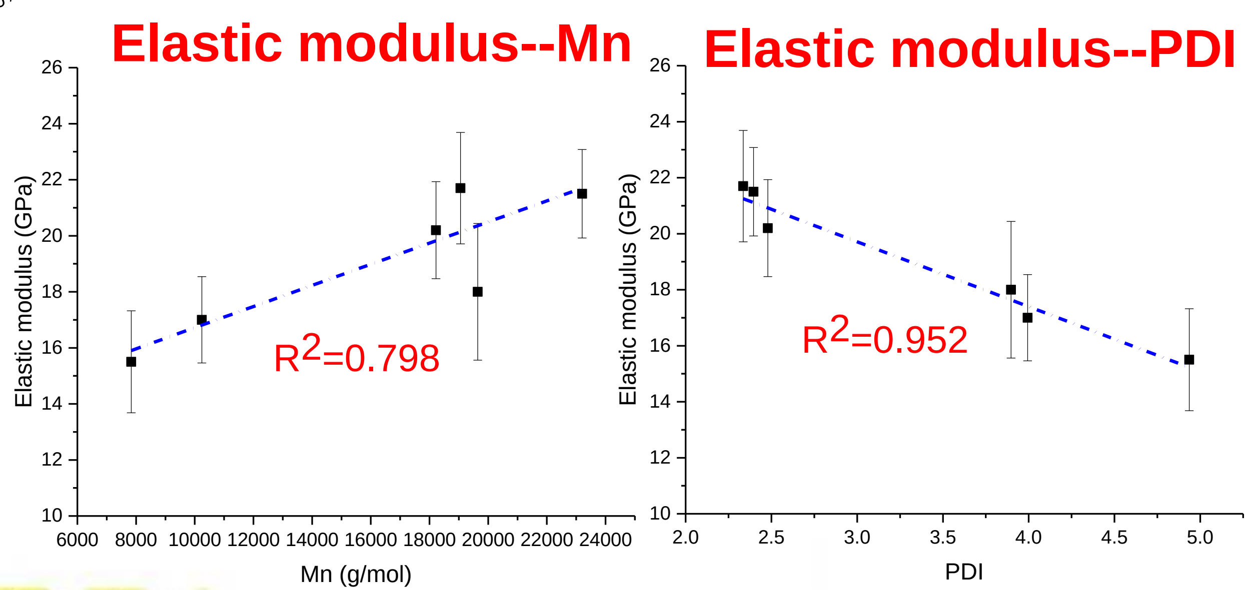
MW: Mixed lignin = 6K; PDI: Mixed lignin > 6K

PDI: Mixed lignin = KL-L/H-Insol.; MW: Mixed lignin > KL-L/H-Insol.

Li, et al., *J. Materials Chemistry A. 2017*. 5, 12740-12746

Molecular Uniformity as the Key to Mechanical Property





Li, et al., *J. Materials Chemistry A. 2017*. 5, 12740-12746

Future work – Summary of impacts of MW on carbon fiber mechanical properties

Two important factors **to improve mechanical properties of lignin-based carbon fiber**

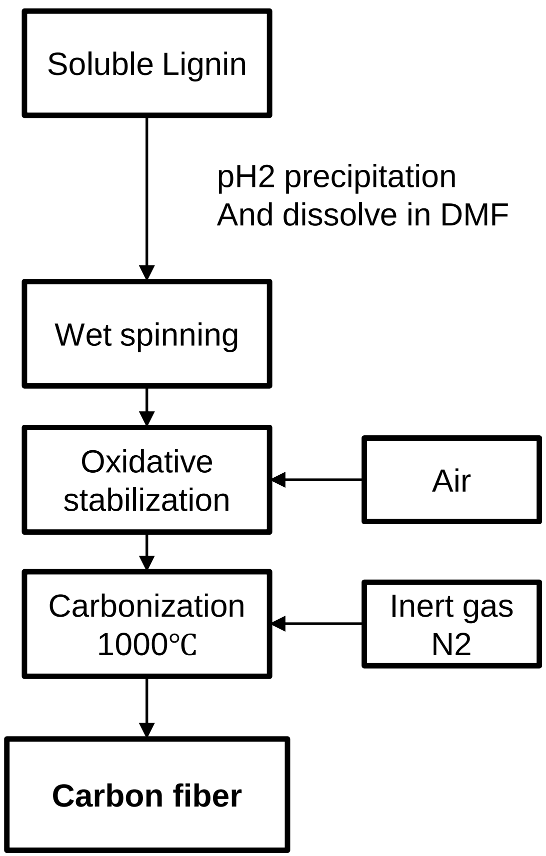
1, Removal of small molecules

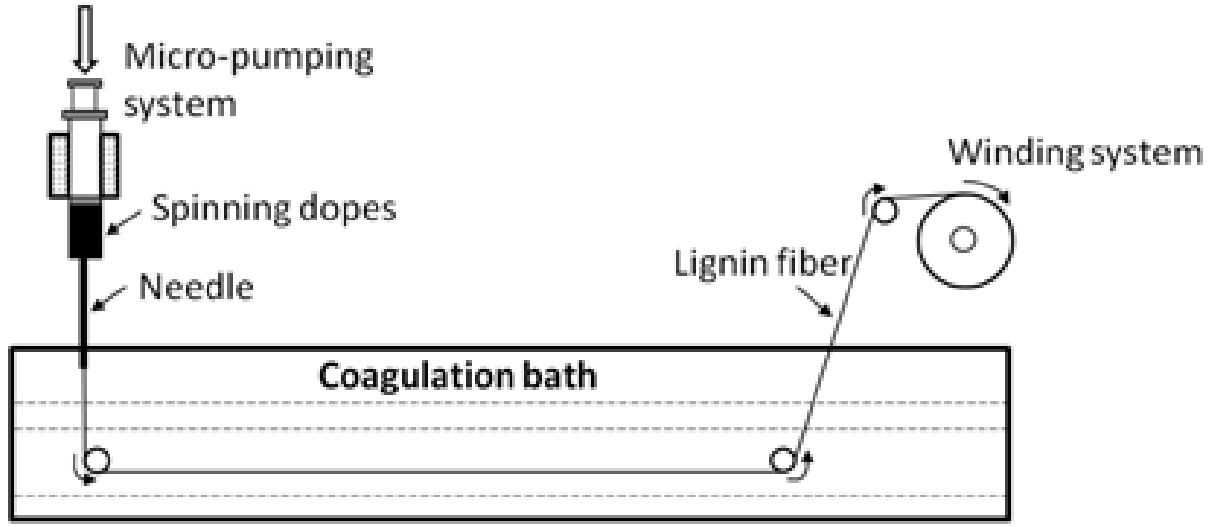
2, Lignin molecular uniformity (low PDI)

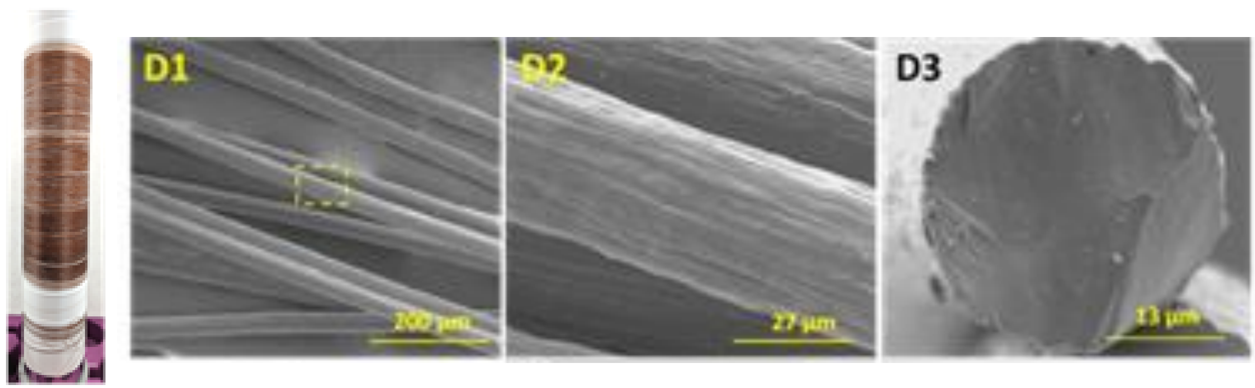
Increase lignin MW from high to very high does not improve elastic modulus. We will design biorefinery procedures accordingly.

Li, et al., *J. Materials Chemistry A. 2017*. 5, 12740-12746

New Wet-Spinning Lignin Carbon Fiber Set-up

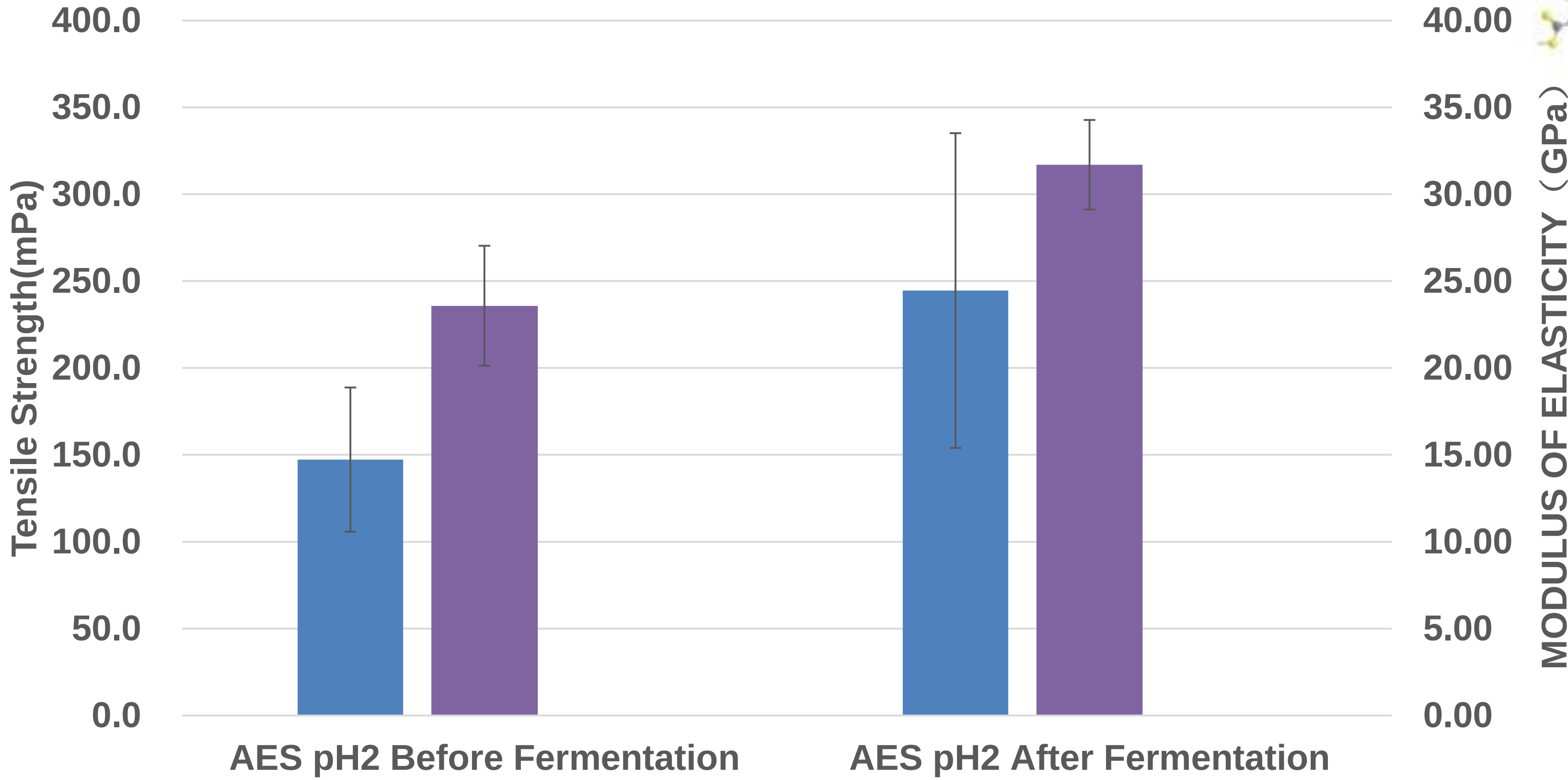






We have developed a proprietorial instrument and process for high quality lignin carbon fiber for future work.

Comparison of Before and After Fermentation

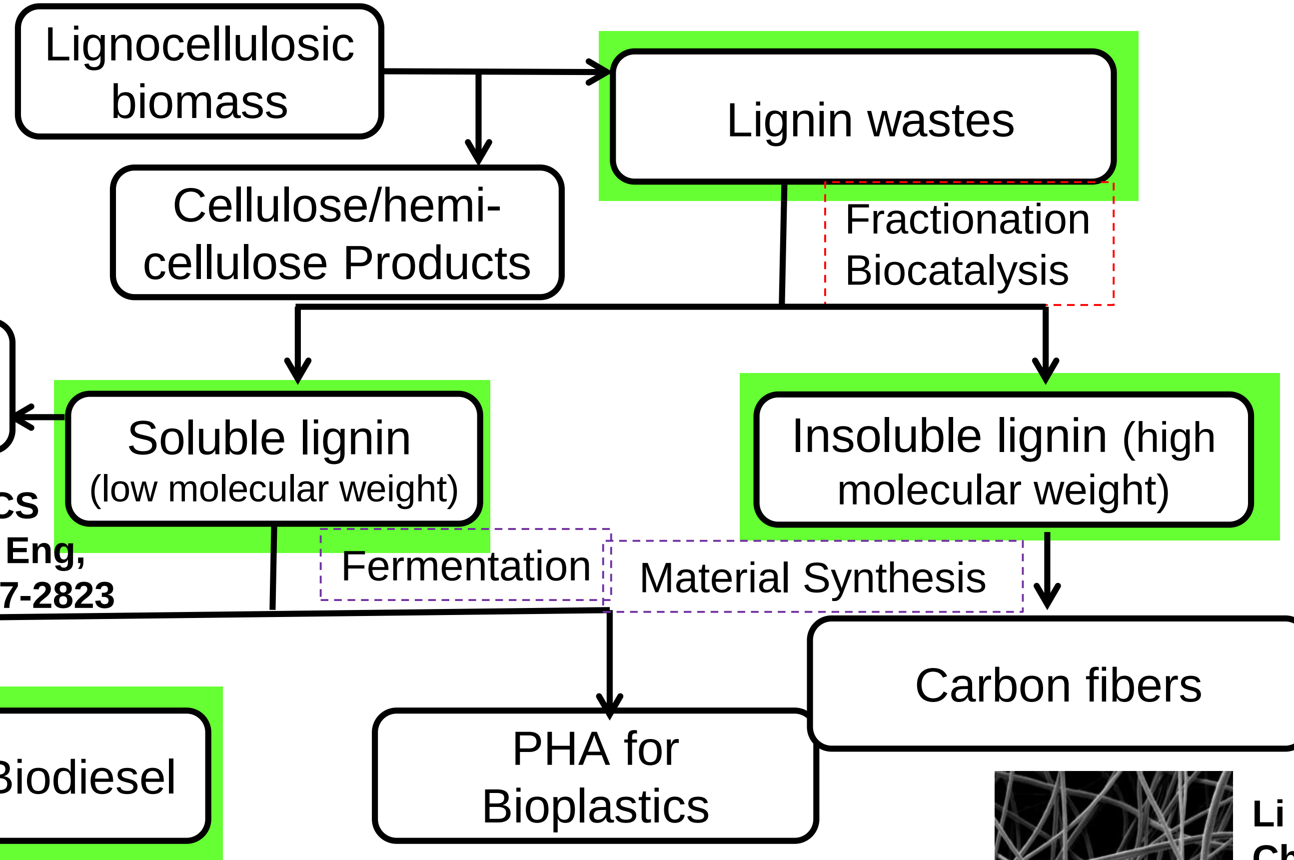


Both tensile strength and modulus of elasticity of after fermentation fiber is better than before fermentation. This means the carbon fiber process can be integrated with fermentation, where the 'waste' lignin from fermentation can be used for carbon fiber.

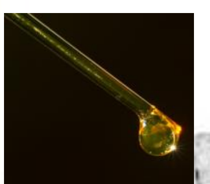
Future Work

- We have advanced fundamental understanding on how lignin uniformity and molecular weight impact carbon fiber performance.
- Based on the knowledge, we will continue to improve carbon fiber mechanical performance using better fractionation technologies with more uniform lignin.
- Based on the knowledge, we have developed integrated processes for multistream integrated biorefinery (MIBR), where the lignin fermentation and carbon fiber manufacturing are integrated.
- We will continue to develop various fractionation technologies and biorefinery configurations to enable the different streams of lignin with various chemical features for different products.

Future Work: Lignin to Pavement Material

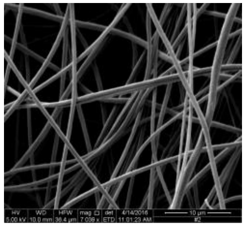


Xie et al., ACS Sus. Chem. Eng, 2017, 5, 2817-2823



Zhao et al., Green Chemistry, 2016, 18, 2802-2810.
Xie et al., ACS Sustainable Chemistry & Engineering, 2017, 5, 2215-2223

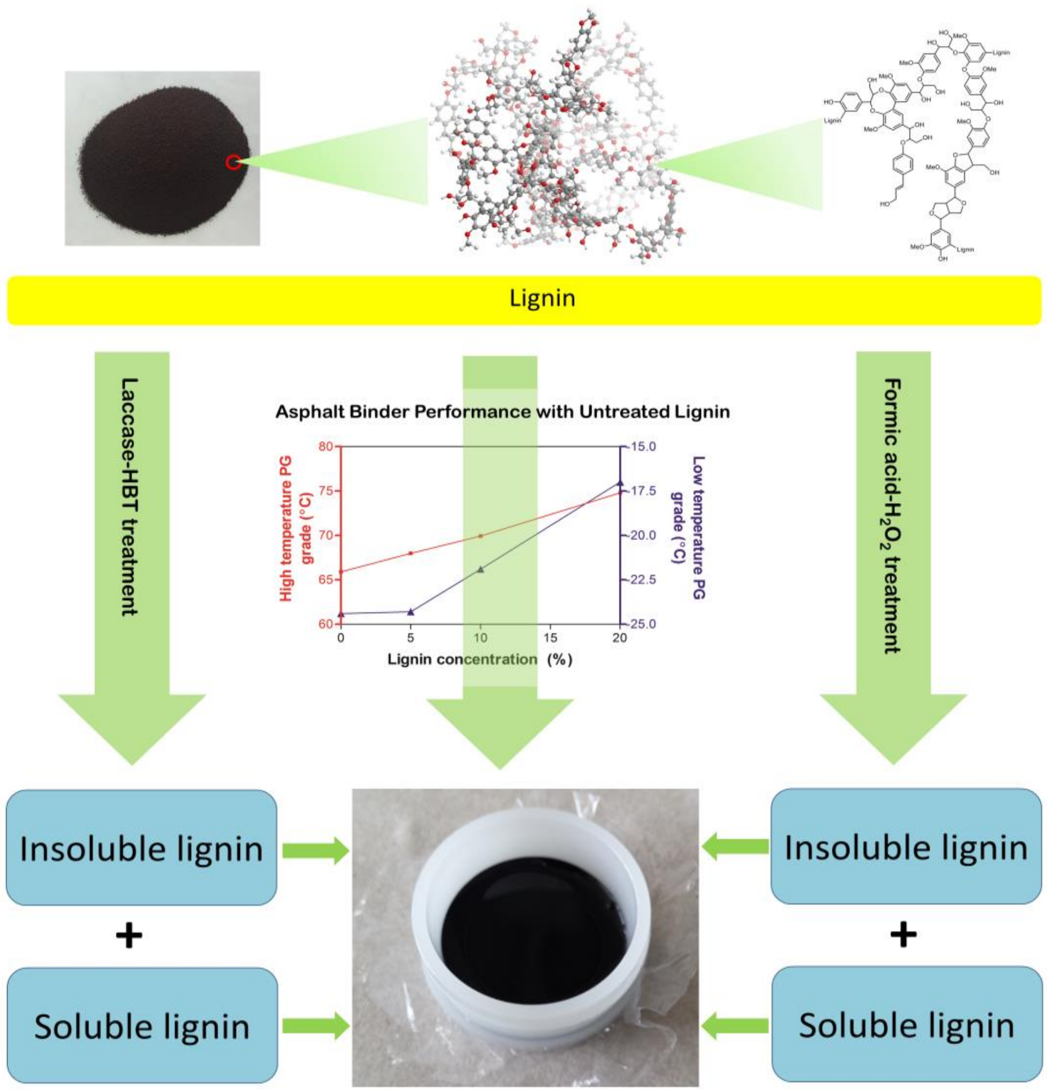
Lin, et al., Green Chemistry, 2016, 18, 5536-5547.
Liu, et al., Green Chemistry, 2017, 19, 4939-4955



Li et al., Green Chemistry, 2017, 19, 1628-1634

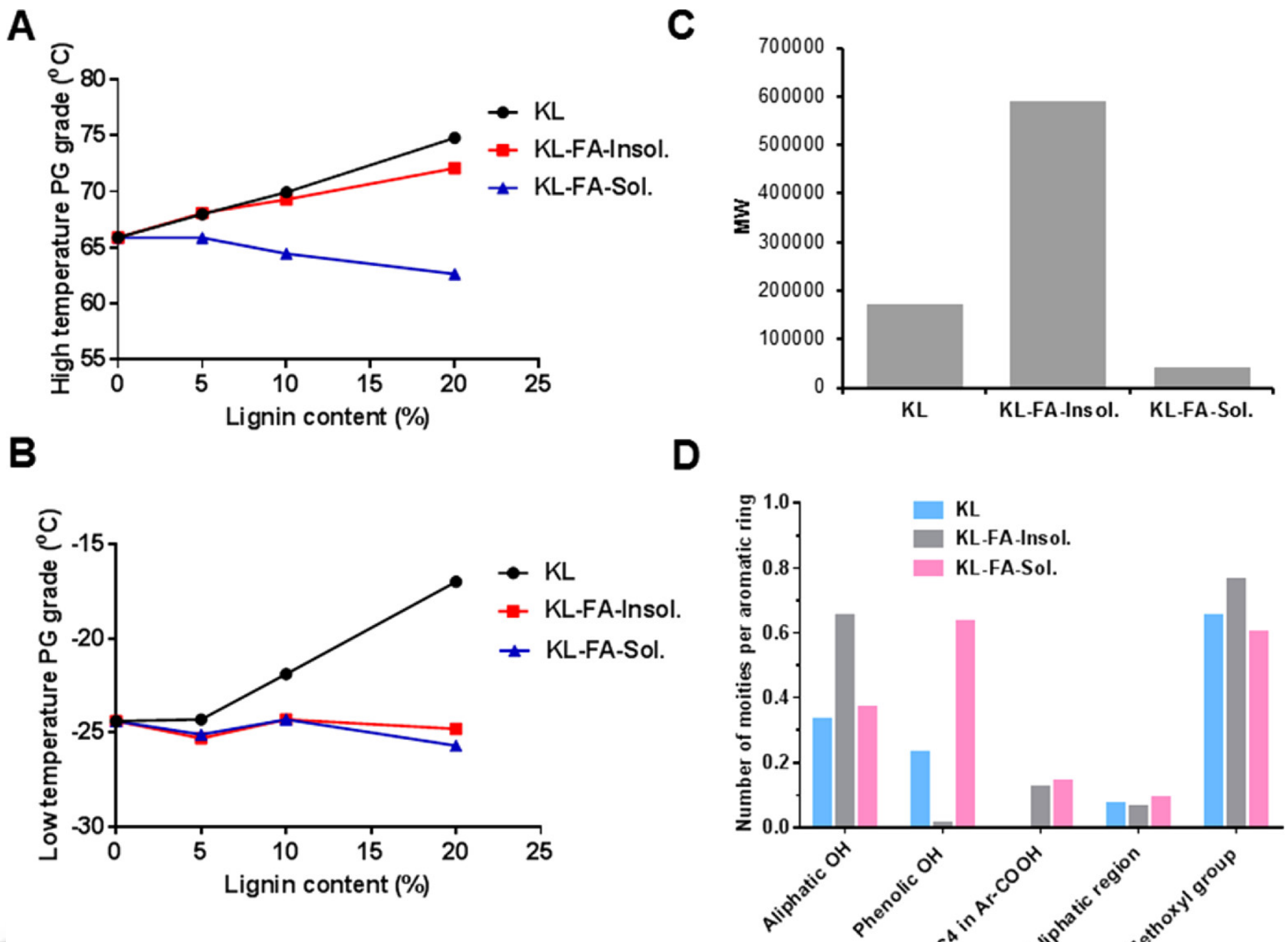
Li et al., J. Materials Chemistry A, 2017, 5, 12740-12746
Li et al., TAPPI J. 2017, 16, 107-108

Unique Asphalt Binder Modifier from Lignin



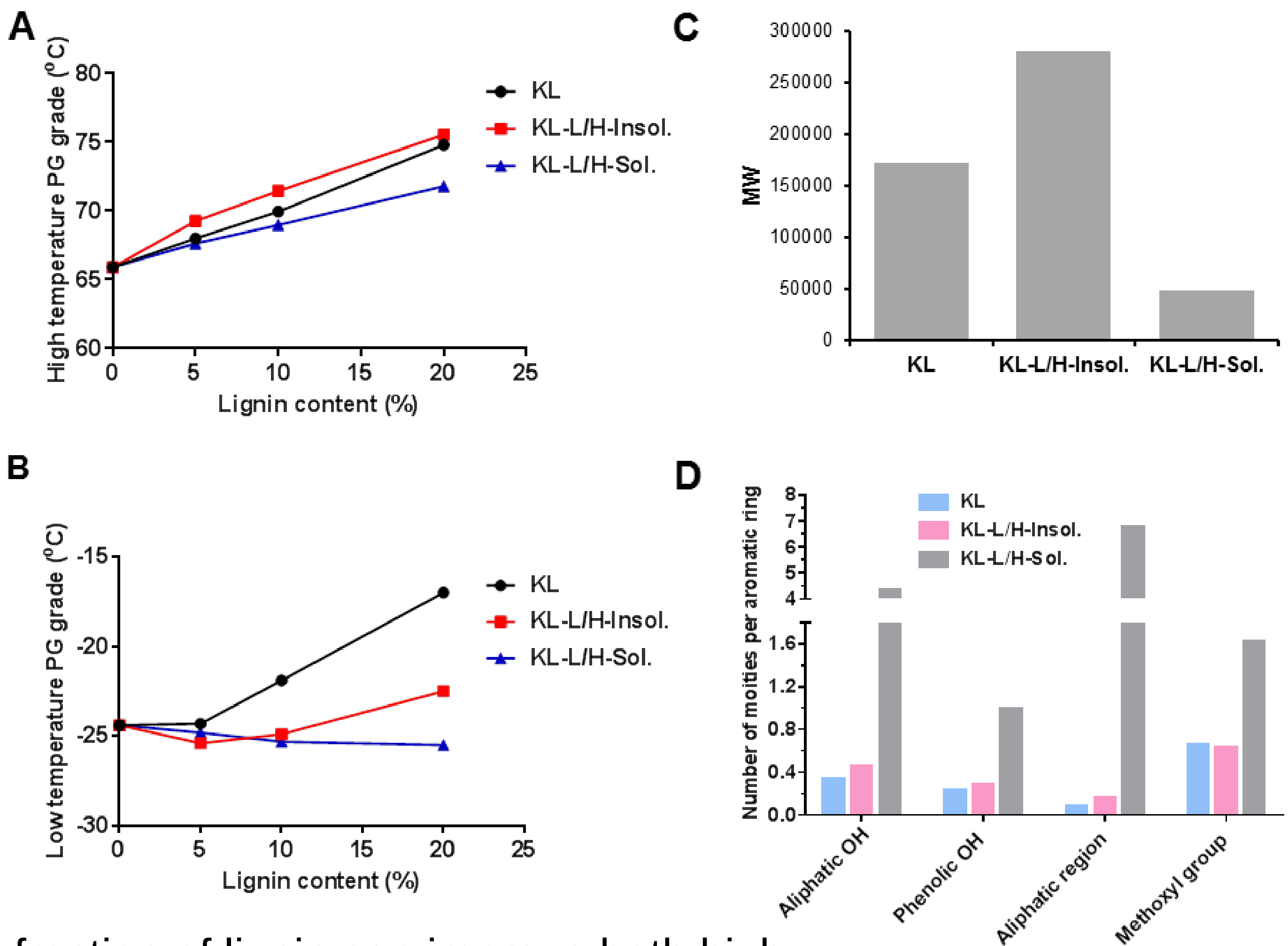
Xie, et al., ACS Sustainable Chemistry & Engineering 2017, 5, 2817-2823

Unique Asphalt Binder Modifier from Lignin



Xie, et al., ACS Sustainable Chemistry & Engineering 2017, 5, 2817-2823

Unique Asphalt Binder Modifier from Lignin



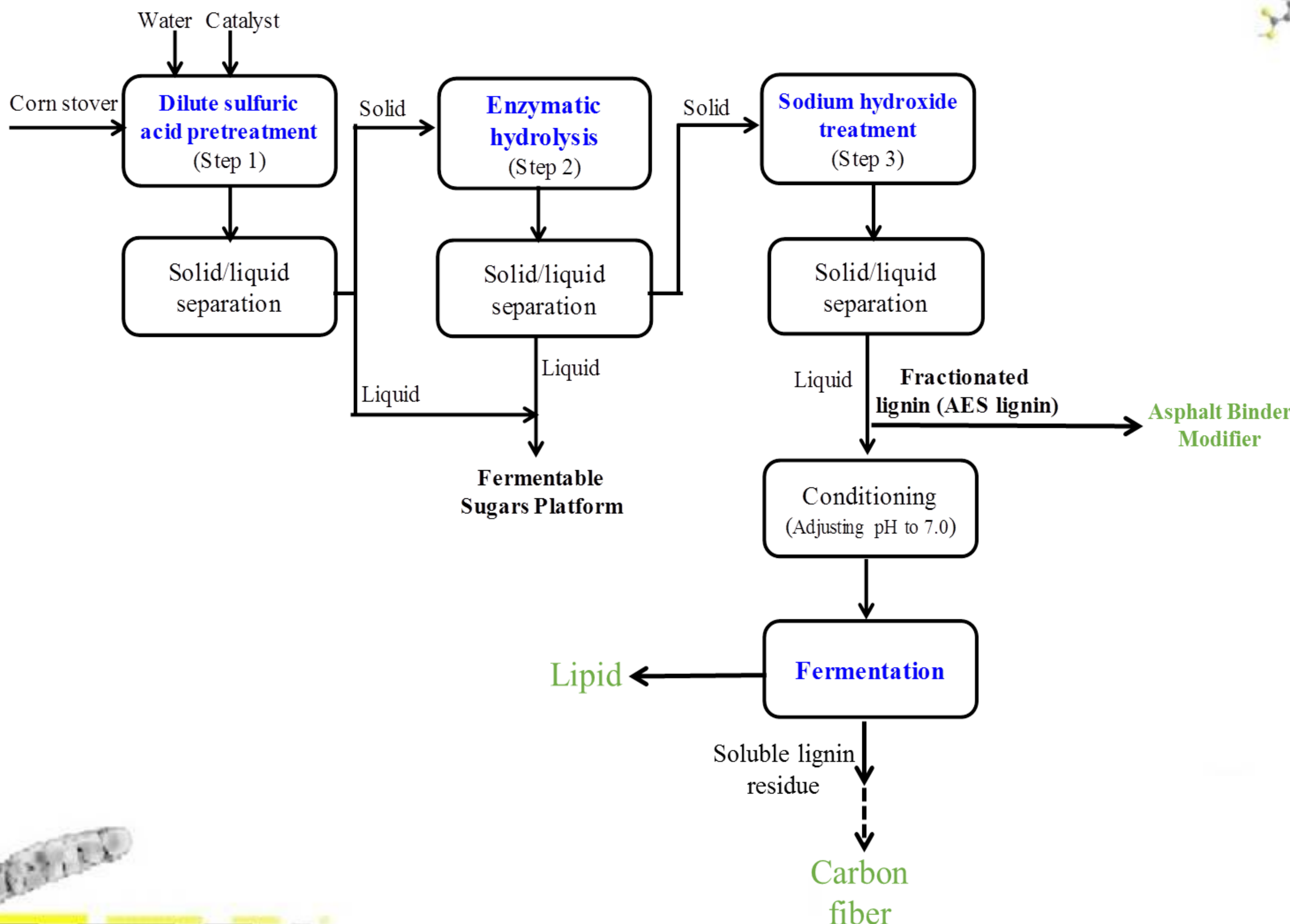
The soluble fraction of lignin can improve both high temperature and low temperature performance.

Xie, et al., ACS Sustainable Chemistry & Engineering 2017, 5, 2817-2823

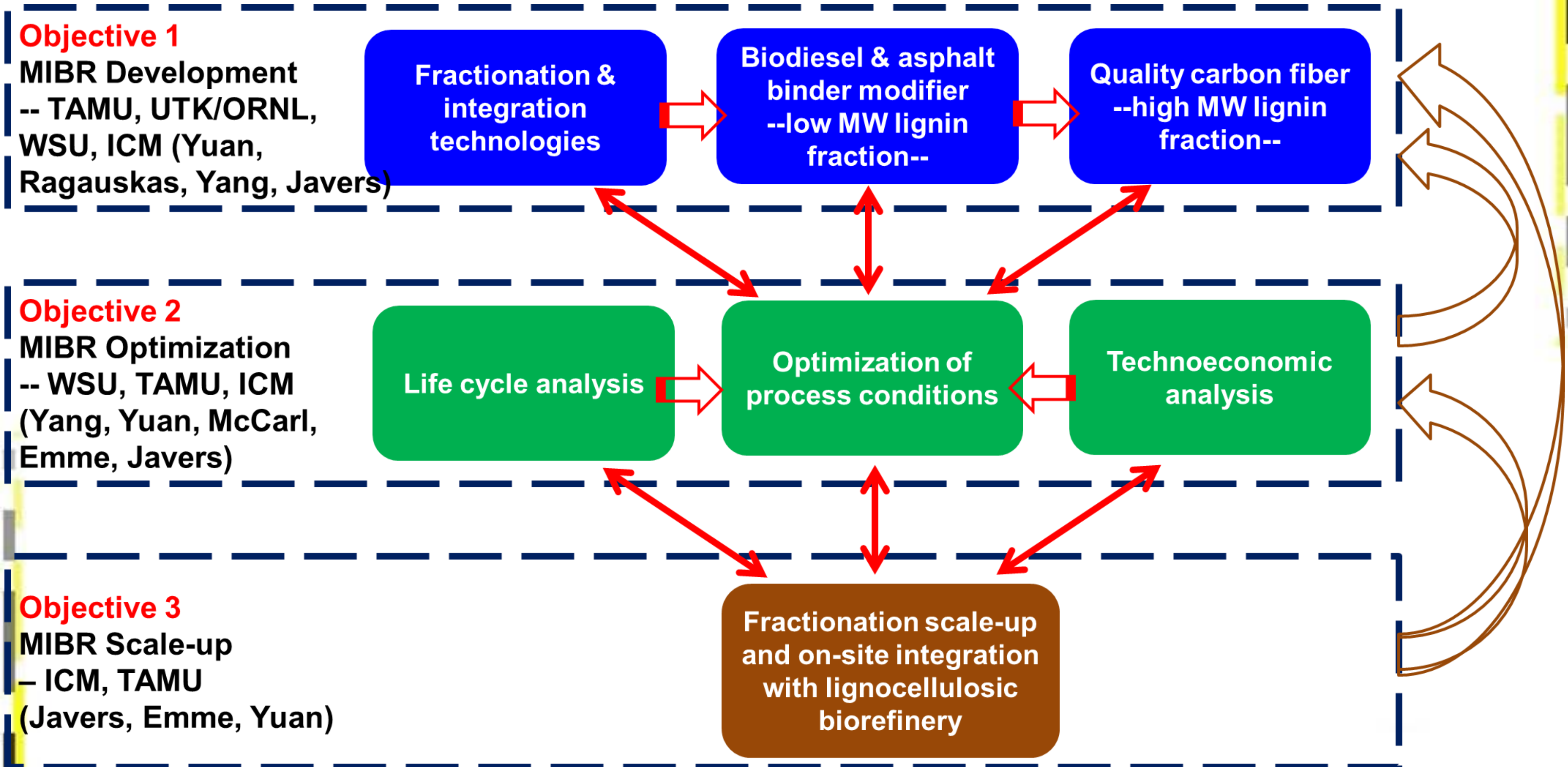
Future Work: Asphalt Binder Modifier

- Lignin can improve the high temperature performance of asphalt binder.
- Depending on the fractionation technology, some lignin fractions can improve high temperature performance, while compromise the low temperature performance. However, some fractions can actually improve both high temperature and low temperature performance.
- AES Lignin has improved high temperature performance.
- During the project, we will develop processing technology to derive the lignin fraction that can improve both high temperature and low temperature performance of asphalt binder, which will be of significant value.

Justification for Future Work



Future Work


Objective 1
MIBR Development
-- TAMU, UTK/ORNL, WSU, ICM (Yuan, Ragauskas, Yang, Javers)
Fractionation & integration technologies
Biodiesel & asphalt binder modifier --low MW lignin fraction--
Quality carbon fiber --high MW lignin fraction--
Objective 2
MIBR Optimization
-- WSU, TAMU, ICM (Yang, Yuan, McCarl, Emme, Javers)
Life cycle analysis
Optimization of process conditions
Technoeconomic analysis
Objective 3
MIBR Scale-up
– ICM, TAMU (Javers, Emme, Yuan)
Fractionation scale-up and on-site integration with lignocellulosic biorefinery

Summary

The project will leapfrog the technologies to enable multi-stream integrated biorefinery (MIBR).

1. Overview – The develop and integrate multiple value-added bioproduct streams to enable multi-stream integrated biorefinery (MIBR) to reduce MESP and improve sustainability and cost-effectiveness of lignocellulosic biorefinery.
2. Approach
   - MIBR Development by Optimizing and Advancing Each Product Process;
   - MIBR Integration and Optimization
   - MIBR Scale-up
3. Technical Accomplishments/Progress/Results
   - The project already made significant progresses to justify future work.
4. Relevance
   - The project is directly addressing MYPP goals.
   - The project provides several product streams to add value to biorefinery.
5. Future work
   - Science-driven approach has been taken to well support the future work.

Acknowledgement

Project Management:

Jay Fitzgerald   Joshua Messner

CoPIs:

Dr. Art Ragauskas   Dr. Bin Yang

Dr. Jeremy Javers   Dr. Brandon Emme

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