Pyroliq 2019: Pyrolysis and Liquefaction of Biomass and Wastes

Proceedings

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Challenges and progresses made on the microkinetic description of lignin liquefaction: Application of group contribution methods

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Challenges and Progresses made on the Micro-kinetic Description of Lignin Liquefaction

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French National Center for Scientific Research (CNRS)

Cork, Ireland, June 17, 2019

The Pioneers

CLASSICAL VIEW OF FAST PYROLYSIS

First experiments in 1970's. Many reactors (fluidized and circulating bed, ablative) were developed and commercialized in the last 40 years. Bio-oil yield over 70 wt. %

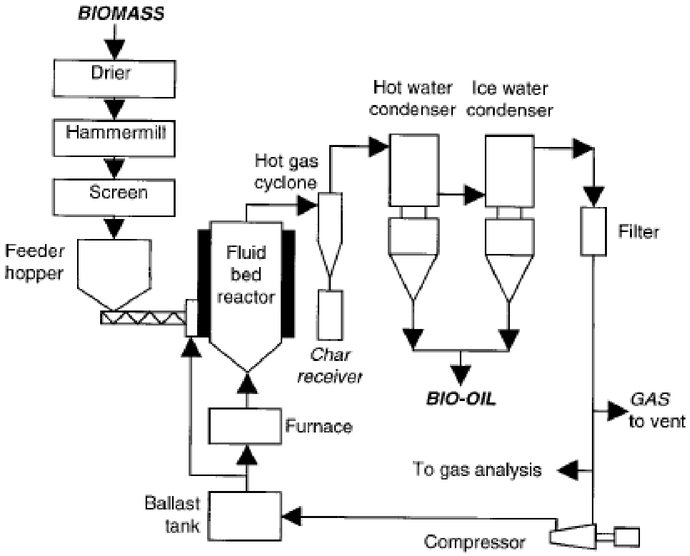
The essential features of fast pyrolysis are:

Very high heating rates that requires a finely ground biomass

Carefully controlled temperature of around 500 ºC

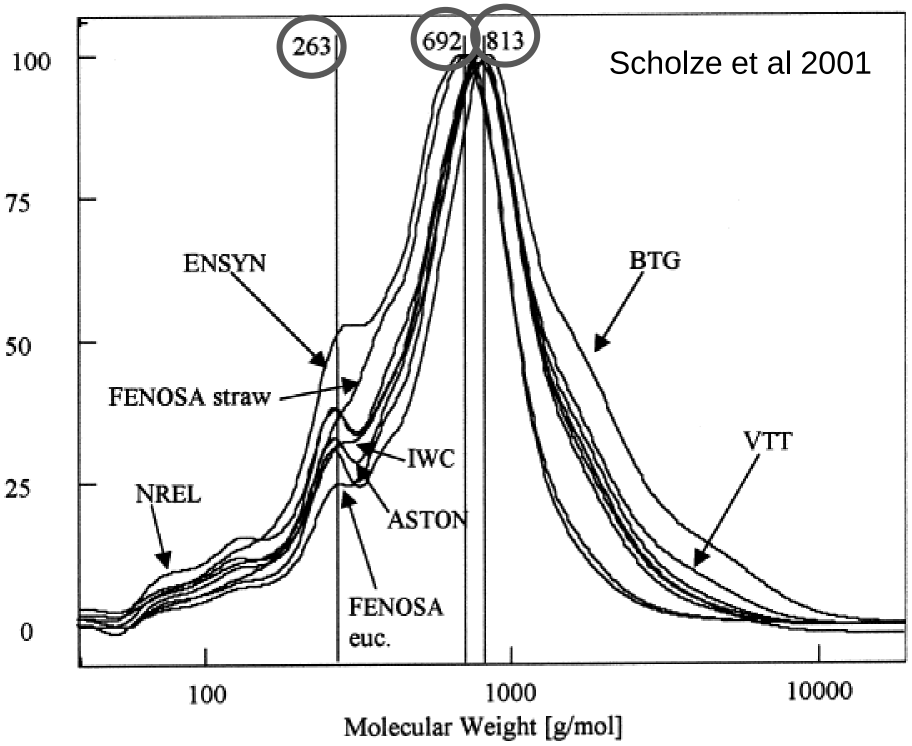
Rapid cooling of the pyrolysis vapors to give the bio-oil product

University of Waterloo Pilot Plant Diagram

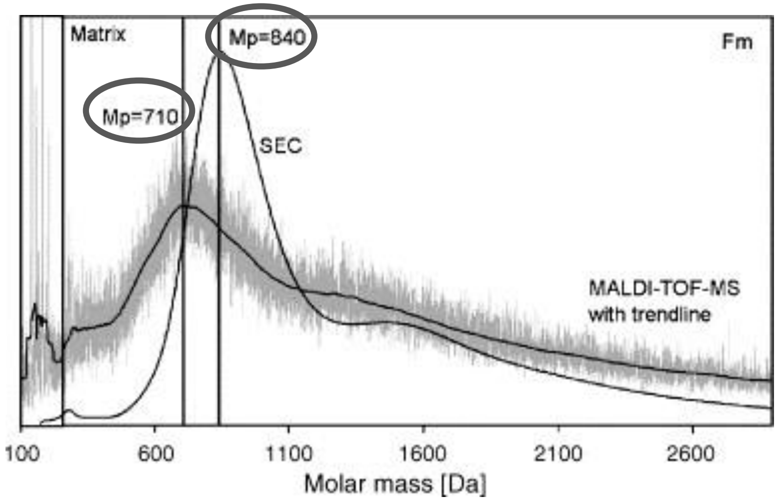


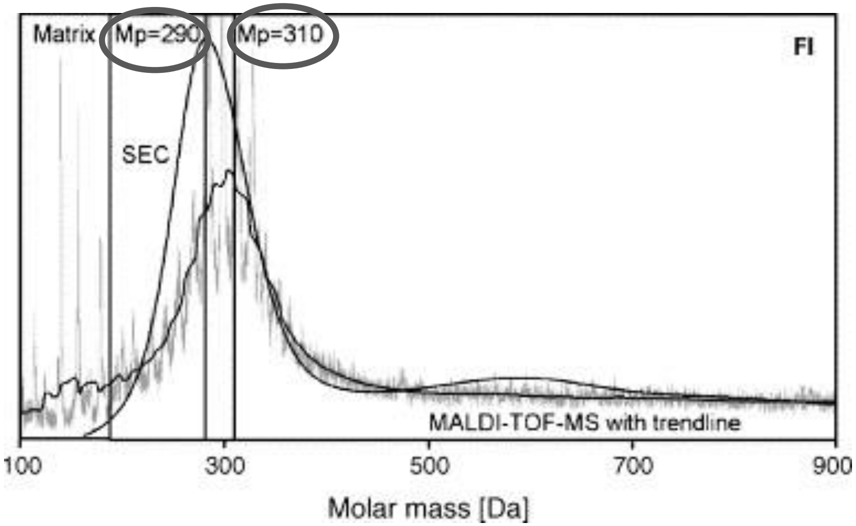
Bridgwater AV, Peacocke GVC: Fast Pyrolysis process for biomass. Renewable and Sustainable Energy Reviews, 4, 2000, 1-73

LIGNIN OLIGOMERIC PRODUCTS



Scholze et al 2001





How to explain the presence of oligomers with (263-310), (692-710) and (813-840) g/mol?

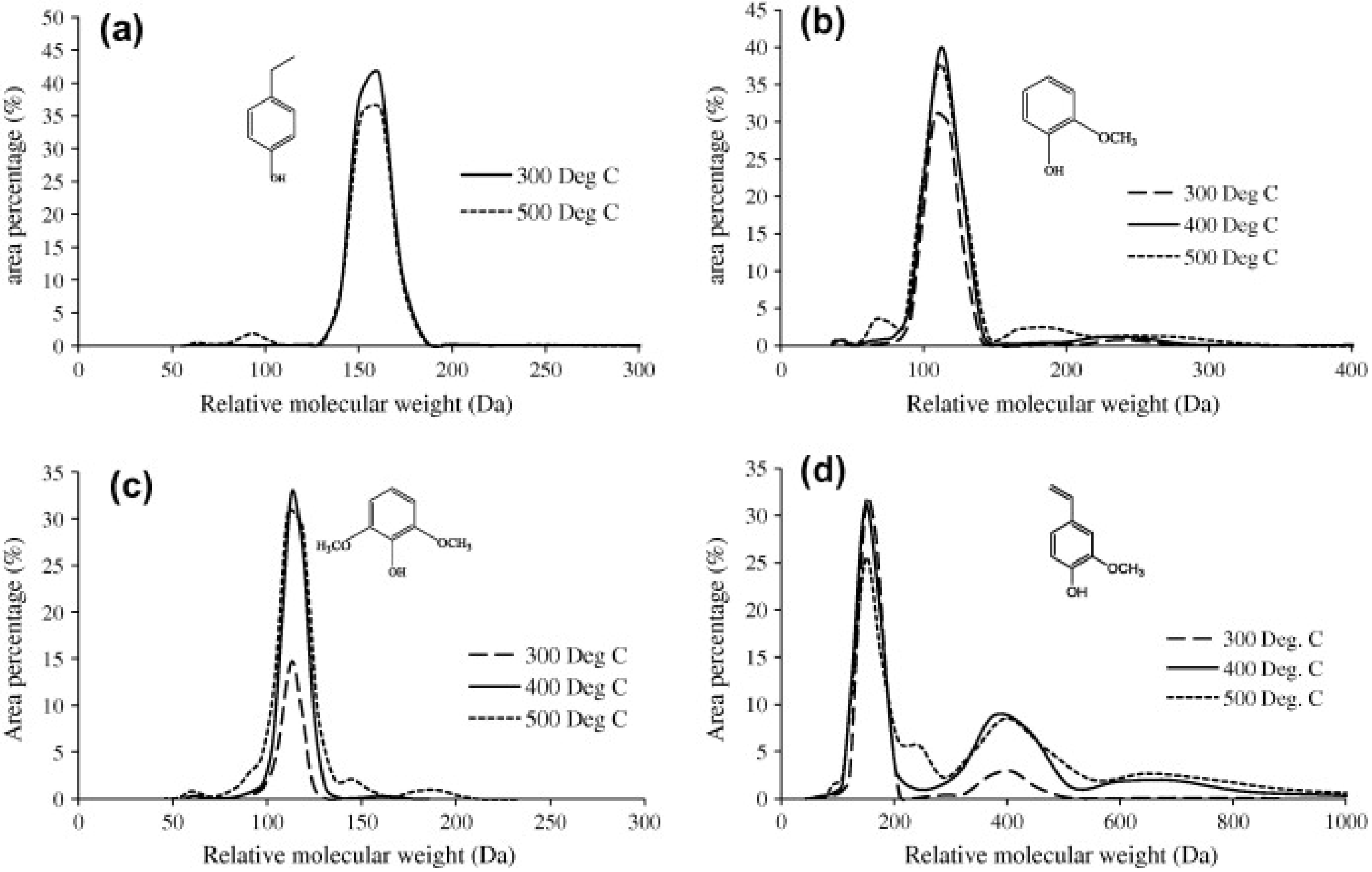
Scholze B, Hensen C, Meier D: Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolysis liquids (pyrolytic lignin): Part II. GPC, carbonyl groups, and ^{13}C-NMR. Journal of Analytical and Applied Pyrolysis, **2001**, 58-59, 387-400

Bayarback R, Dy Nguyen V, Schurr U, Meier D: Characterization of the wáter insoluble fraction from fast pyrolysis liquids (pyrolysis lignin): Part III. Molar mass characteristics by SEC, MALDI-TOF-MS, LDI-TOF-MS and Py-FIMS. . Journal of Analytical and Applied Pyrolysis, **2001**, 58-59, 387-400

FORMATION OF OLIGOMERS

According to **Iowa State** monomers are the main products of pyrolysis reactions. Oligomers are formed by thermochemical reactions.

Formation of lignin oligomers from monomers



Iowa State Group: Some oligomers in pyrolysis oil form from the recombination of monomeric products!

Bai X, Kim KH, Brown RC, Dalluge E, Hutchinson C, Lee YJ, Dalluge D: Formation of phenolic oligomers during fast pyrolysis of lignin. Fuel Vol. 128, 2014, 170-179

Experimental evidences to create realistic physical models

BIO-OIL CHARACTERIZATION

Overall Bio-oil composition in terms of Functional Groups

Sample	Water OH	Total Carbonyl groups	Total Phenols				Total Carboxylic acids		Total Aliphatic OH
	KF Titration [mmol/g]	Titration [mmol/g]	FC [mmol/g]	Titration [mmol/g]	^{31}P-NMR [mmol/g]	^{1}H-NMR [mmol/g]	Titration [mmol/g]	^{31}P-NMR [mmol/g]	^{31}P-NMR [mmol/g]
BTG	14.6	4.2	1.8	1.9	1.7	0.98	1.3	0.7	4.2
Amaron	10.3	4.8	2.1	2.1	1.2	1.50	2.1	0.9	4.0
15A	9.7	5.3	2.2	2.8	0.9	1.17	1.9	1.0	5.0
16A	15.9	4.8	1.6	1.9	1.1	0.92	1.8	1.1	4.4
17A	15.7	4.6	1.9	2.2	1.3	1.18	1.7	1.1	4.0
18A	17.1	4.4	2.0	2.3	1.6	1.05	1.5	1.1	4.2
19A	16.6	4.5	2.1	2.4	1.3	1.28	1.2	0.7	3.3
20A	7.8	4.8	3.1	3.9	1.7	1.90	1.1	0.5	3.5
21A	16.6	4.7	2.1	2.2	1.8	1.24	1.2	0.8	4.2
22A	13.4	4.8	2.3	2.7	1.5	1.67	1.1	0.5	3.5

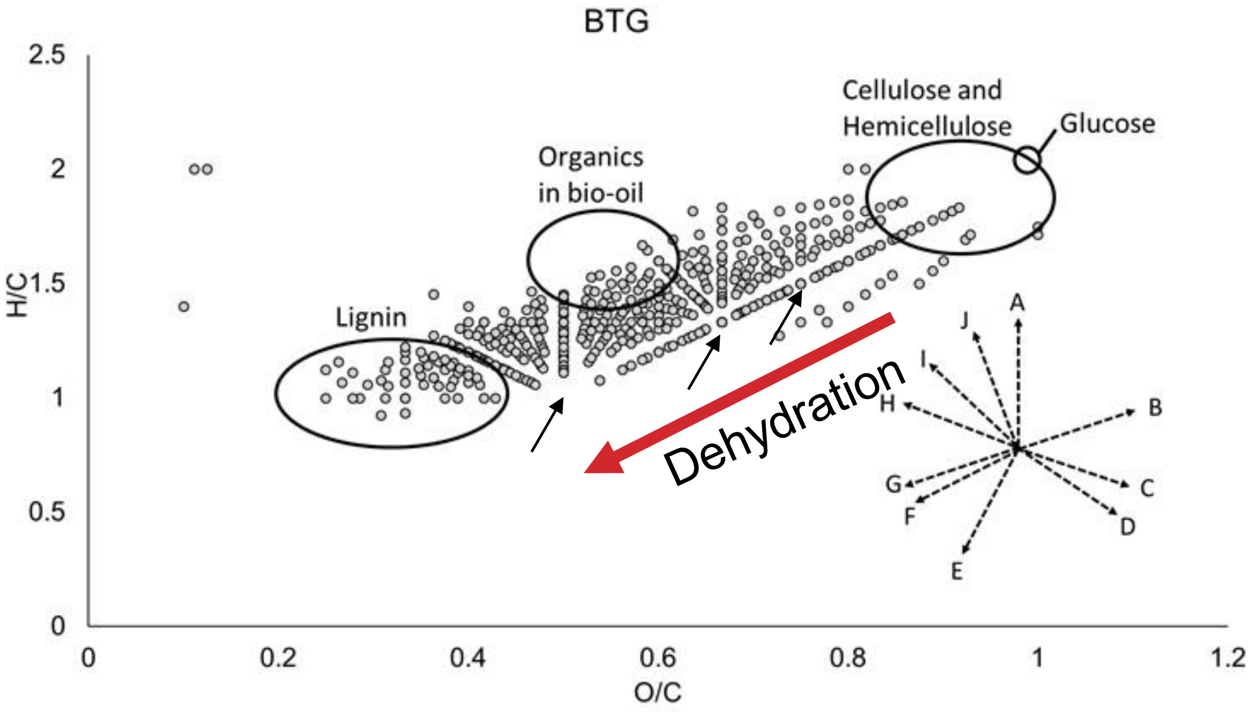
Total Oil	**7.8-16.6**	**4.2-5.3**	**0.9-3.9**	**0.5-2.1**	**3.3-5.0**
Volatiles (GC/MS)	**7.8-16.6**	**1.6-3.6**	**0.1-0.3**	**0.7-1.3**	**2.4-4.5**

Stankovikj F, McDonald A, Helms GL, Garcia-Perez: Quantification of Bio-oil Functional Groups and Evidences of the Presence of Pyrolytic Humins. Energy Fuels, 2016, 30 (8), 6505-6524

Stankovikj F, McDonald A, Helms GL, Olarte MV, Garcia-Perez M: Characterization of Biomass Pyrolysis Oils's Water Soluble Fraction. Accepted in Energy and Fuels, 2017

BIO-OIL CHARACTERIZATION

FTICR-MS (Van Krevelen plot of non-volatile fraction of the BTG bio-oil)



More work is needed to describe the reactions in liquid intermediate. The lines observed in Van Krevelen plots present opportunities to describe the secondary reactions

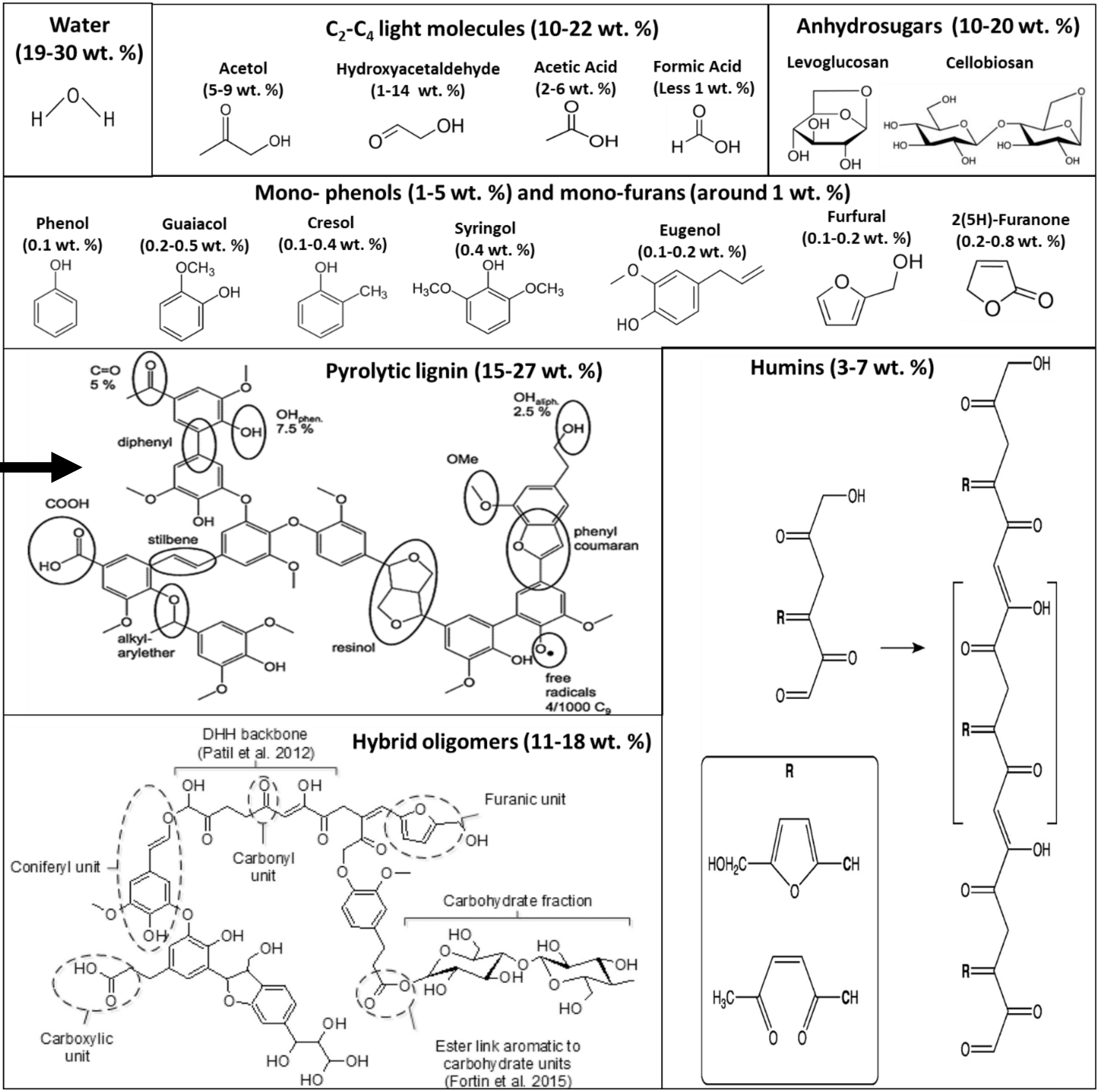
(A) Removal of Levoglucosan, **(B)** Removal of Furan, **(C)** removal of Acetol, **(D)** removal of methane **(E)** demethoxylationdehydration **(F)** dehydration, **(G)** removal of glycoaldehyde **(H)** deraboxylation **(J)** decarbonylation

Stankovikj F, McDonald A, Helms GL, Garcia-Perez: Quantification of Bio-oil Functional Groups and Evidences of the Presence of Pyrolytic Humins. Energy Fuels, 2016, 30 (8), 6505-6524

Stankovikj F, McDonald A, Helms GL, Olarte MV, Garcia-Perez M: Characterization of Biomass Pyrolysis Oils's Water Soluble Fraction. Paper in Preparation to be submitted to Energy and Fuels, 2016

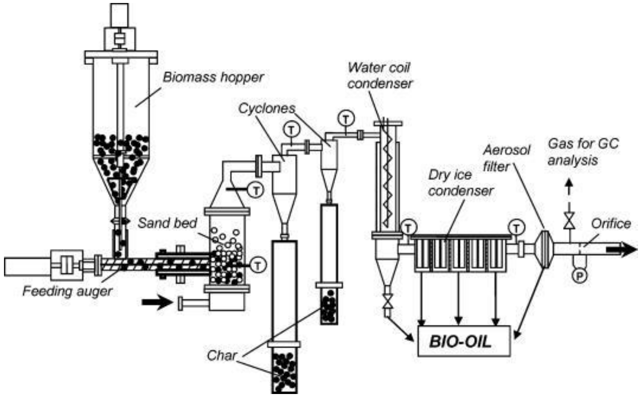
BIO-OIL CHARACTERIZATION

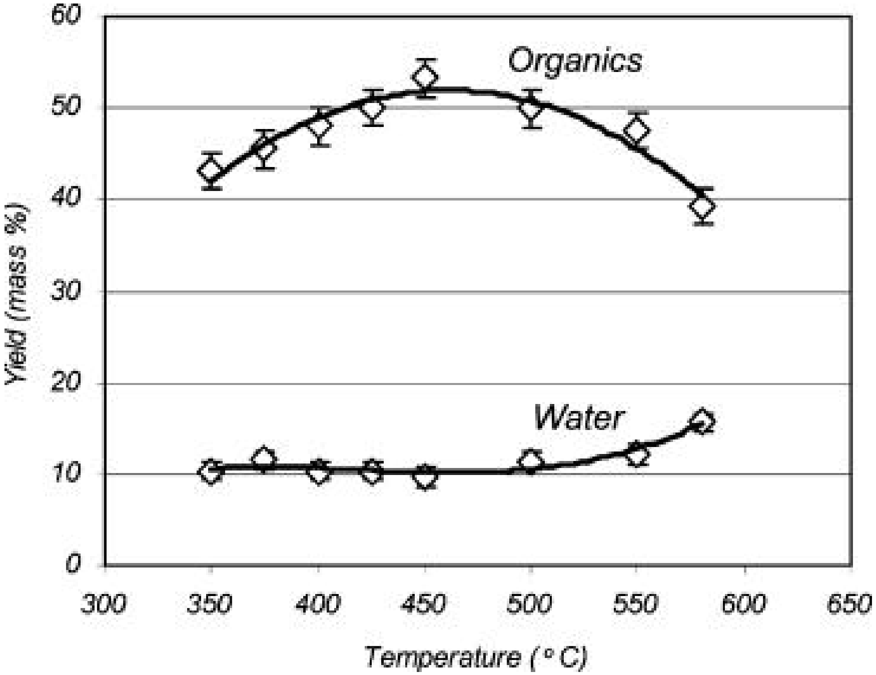
How are these products formed?

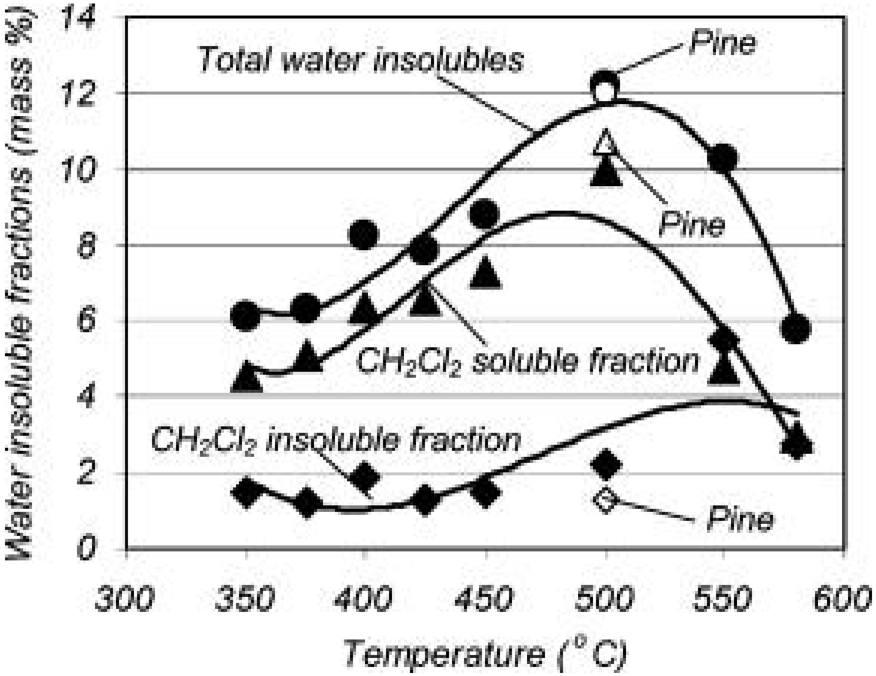


LIGNIN OLIGOMERIC PRODUCTS

EFFECT OF PYROLYSIS TEMPERATURE (Monash University, Chun-Zhu Li's group) (2008)



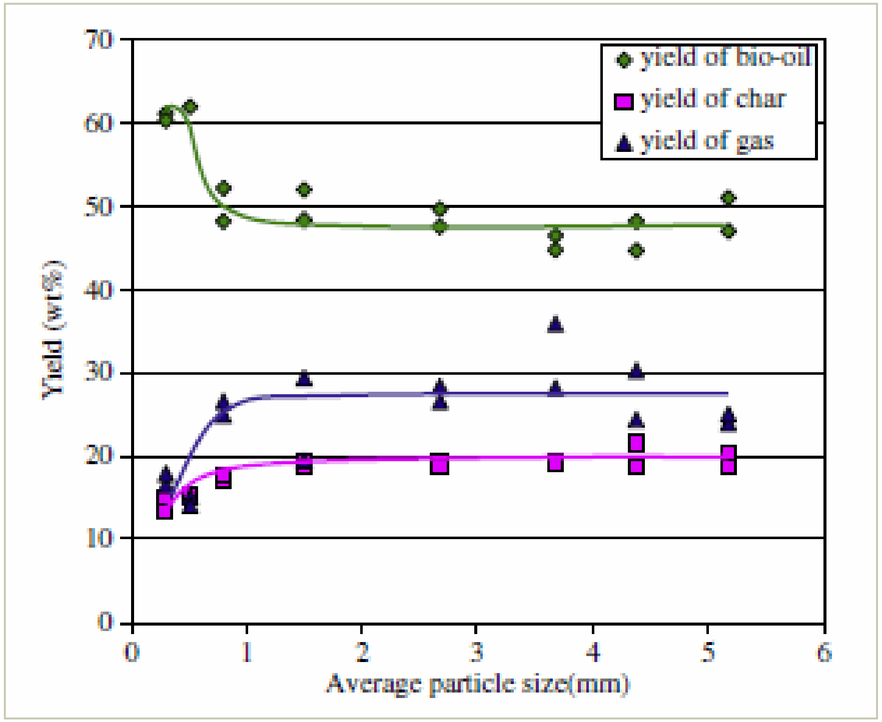


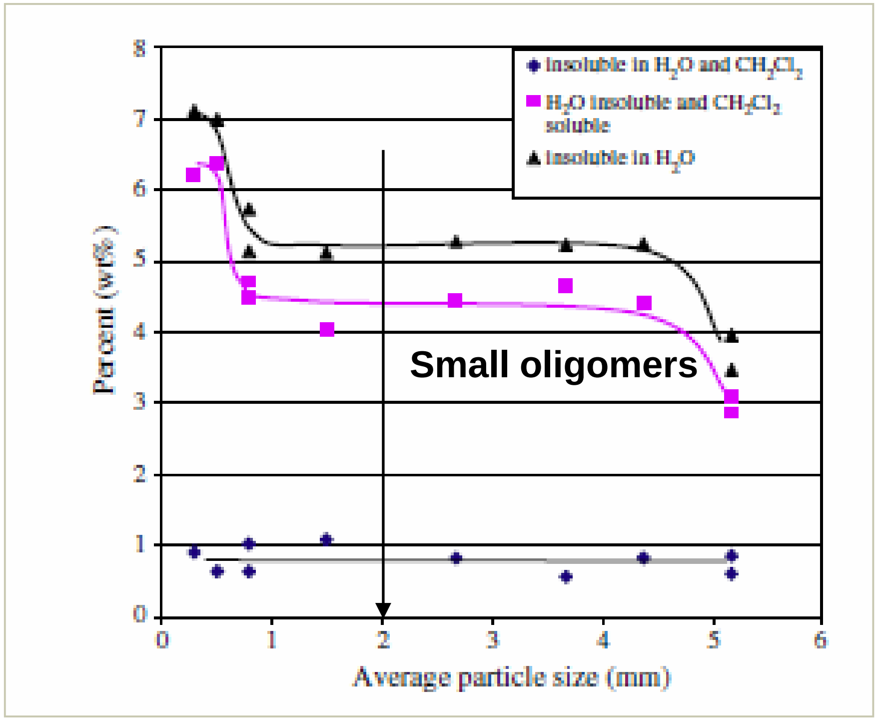


Garcia-Perez M, Wang XS, Shen J, Rhodes MJ, Tian F, Lee W-J, Wu H, Li C-Z: Fast Pyrolysis of Oil Mallee Woody Biomass: Effect of Temperature on the Yield and Quality of Pyrolysis Products. Ind. Eng. Chem. Res. **2008**, 47, 1846-1854

LIGNIN OLIGOMERIC PRODUCTS

EFFECT OF PARTICLE SIZE (Chun-Zu Li's group, Monash University) (2009)

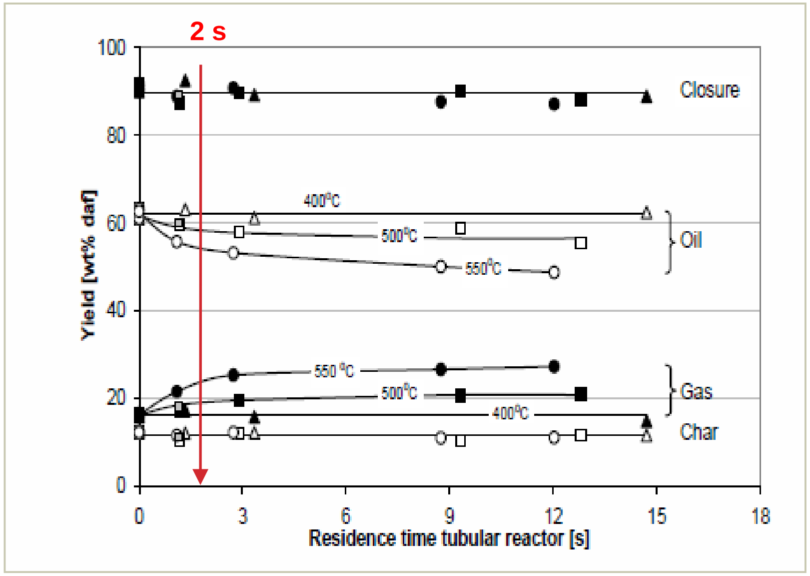


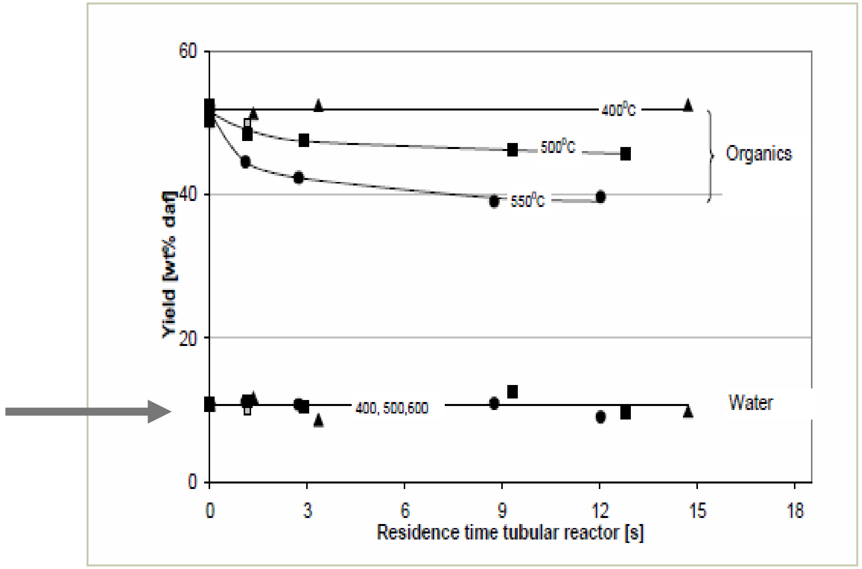


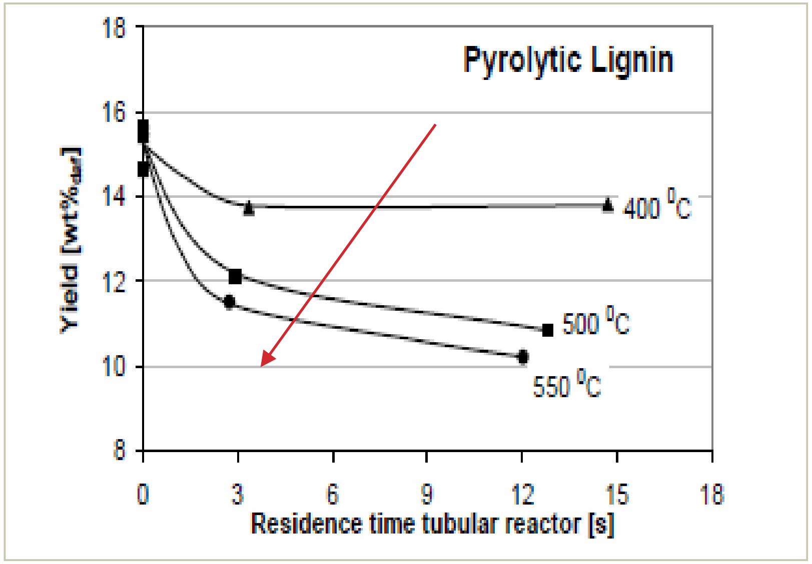
Shen J, Wang X-S, Garcia-Perez M, Mourant D, Rhodes MJ, Li C-Z: Effects of particle size on the fast pyrolysis of oil malee woody biomass. Fuel 88 (2009) 1810-1817

LIGNIN OLIGOMERIC PRODUCTS

EFFECT OF VAPORS RESIDENCE TIME INSIDE THE PYROLYSIS REACTOR (University of Twente) (2011)



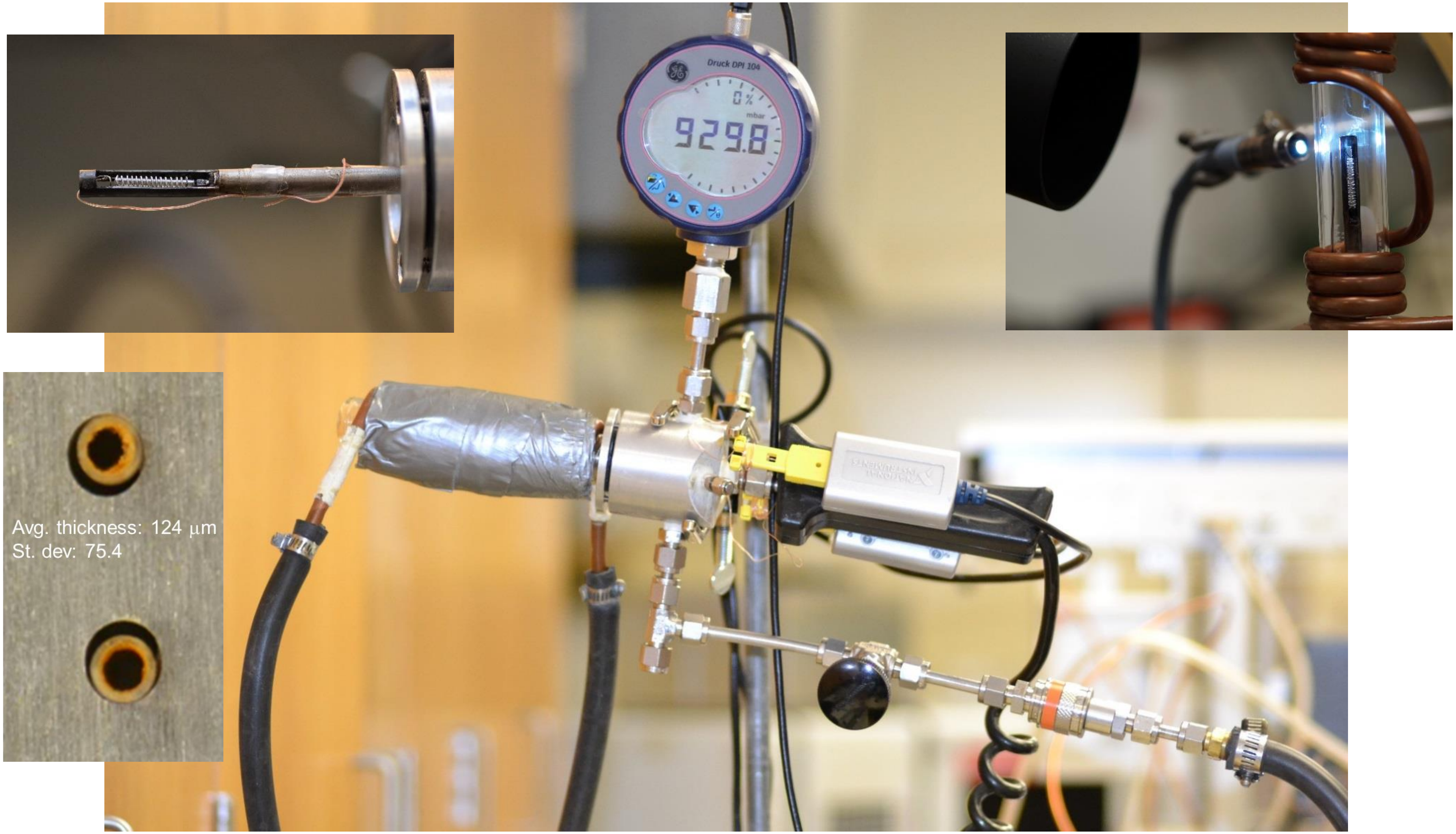




Roel JM Westerhof: Refining Fast Pyrolysis of Biomass. PhD Thesis University of Twente 2011

LIGNIN OLIGOMERIC PRODUCTS

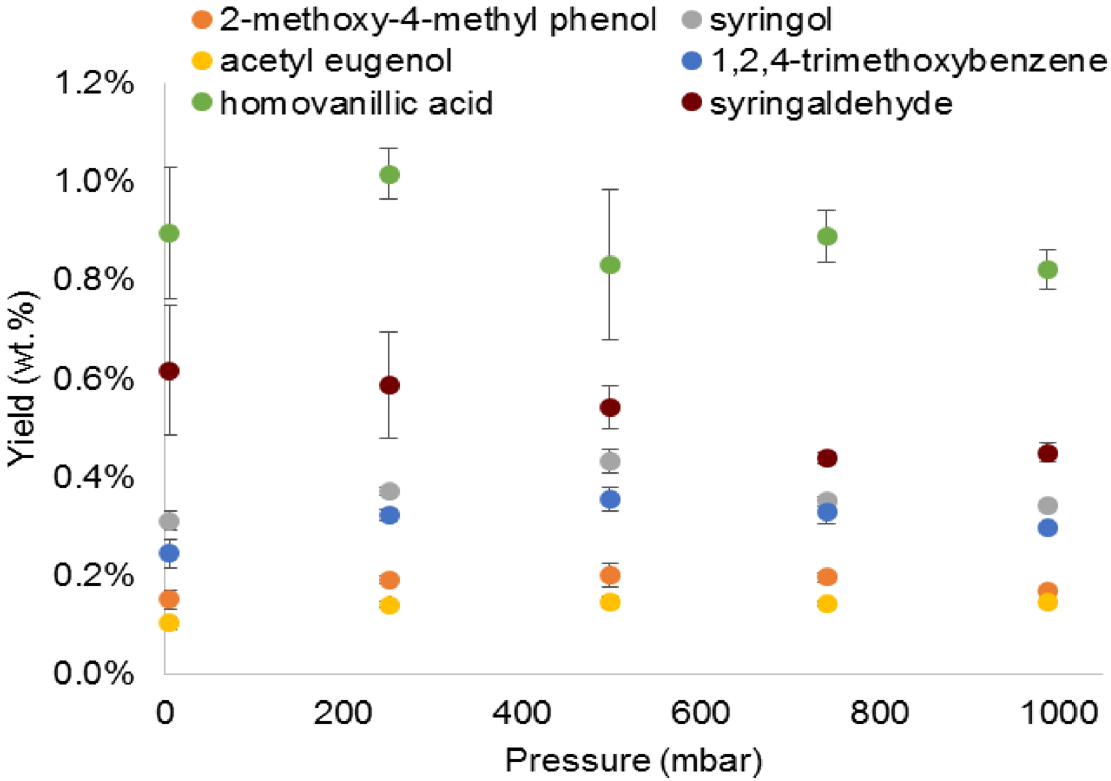
Captive Sample Pyroprobe Reactor (Effect of Pressure)

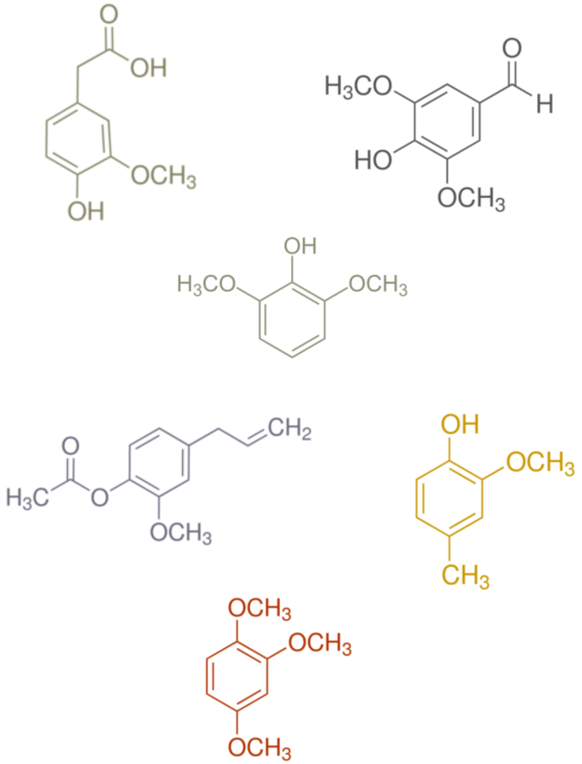


Pecha B, Montoya JI, Ivory C, Chejne F, Garcia-Perez M: Modified Pyroprobe Captive Sample Reactor: Characterization of Reactor and Cellulose Pyrolysis at Vacuum and Atmospheric Pressures *Industrial and Engineering Chemistry Research*, **2017**, 56 (18), 5185-5200

LIGNIN OLIGOMERIC PRODUCTS

Effect of pressure on the production of monomeric compounds



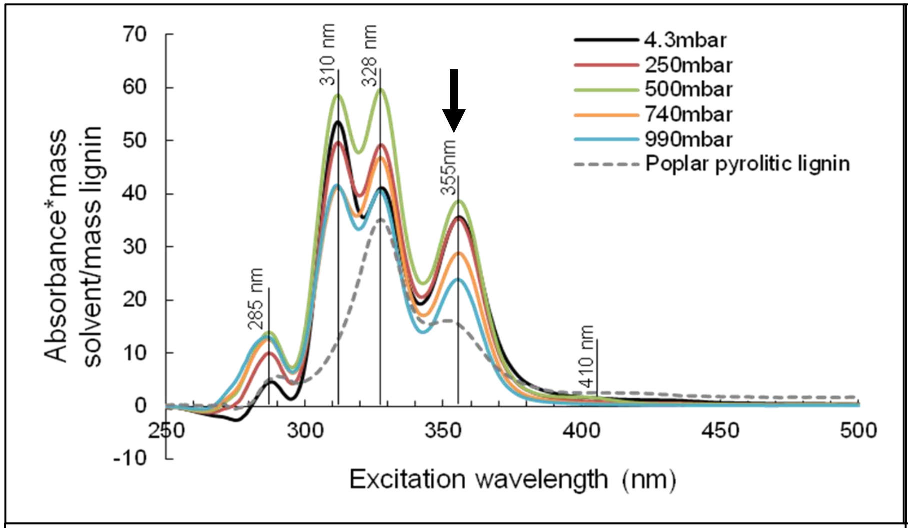


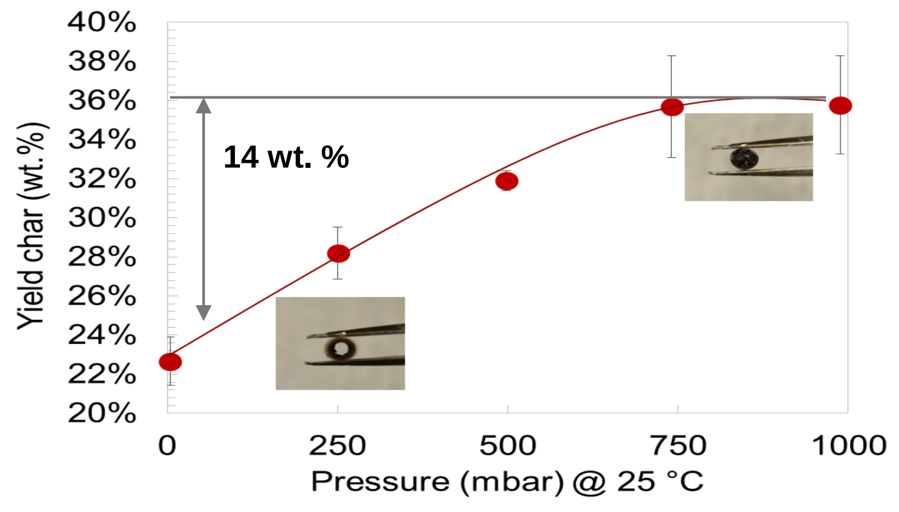
Small quantities of monomeric phenols are formed by primary reactions. The reactions in the liquid intermediate do not lead to additional monomeric products (cracking reactions in the liquid intermediate have limited importance). Most of the lignin is depolymerized into oligomeric products!

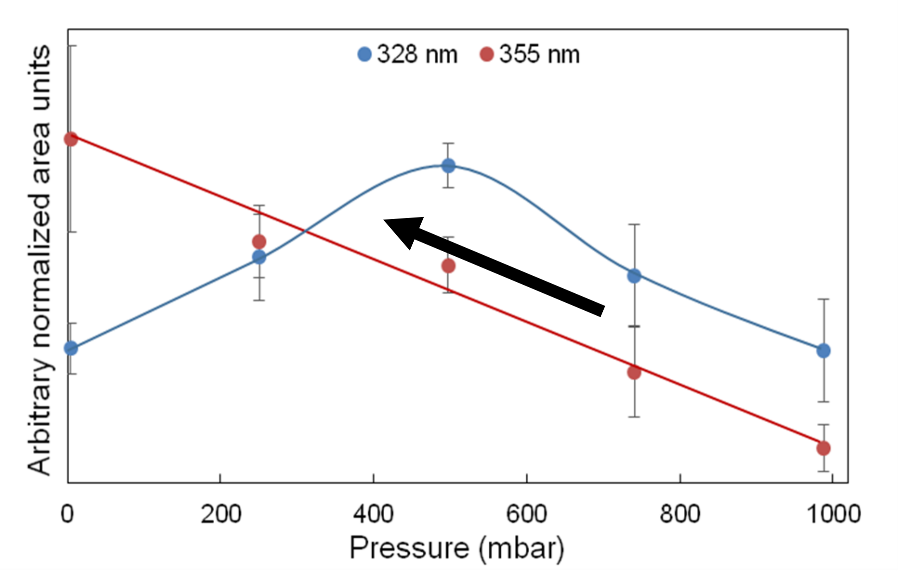
Pecha B, Terrel E, Montoya JI, Chejne F, Garcia-Perez M: Effect of pressure on pyrolysis of milled Wood lignin and acid washed hybrid poplar Wood. Industrial and Engineering chemistry research, **2017,** , 56 (32), pp 9079–9089

LIGNIN OLIGOMERIC PRODUCTS

EFFECT OF PRESSURE







Addition reactions in the liquid intermediate are very important and lead to the formation of large polyaromatic ring systems (char).

Pressure is directly related with evaporation it does not impact reactions in liquid intermediate!

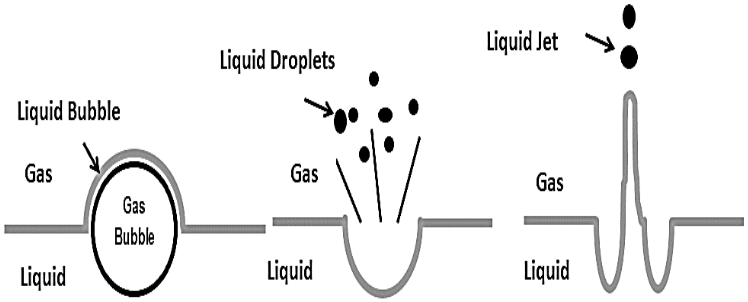
Pecha B, Terrel E, Montoya JI, Chejne F, Garcia-Perez M: Effect of pressure on pyrolysis of milled Wood lignin and acid washed hybrid poplar Wood. Industrial and Engineering Chemistry Research, **2017,** 56, 32, 9079-9089

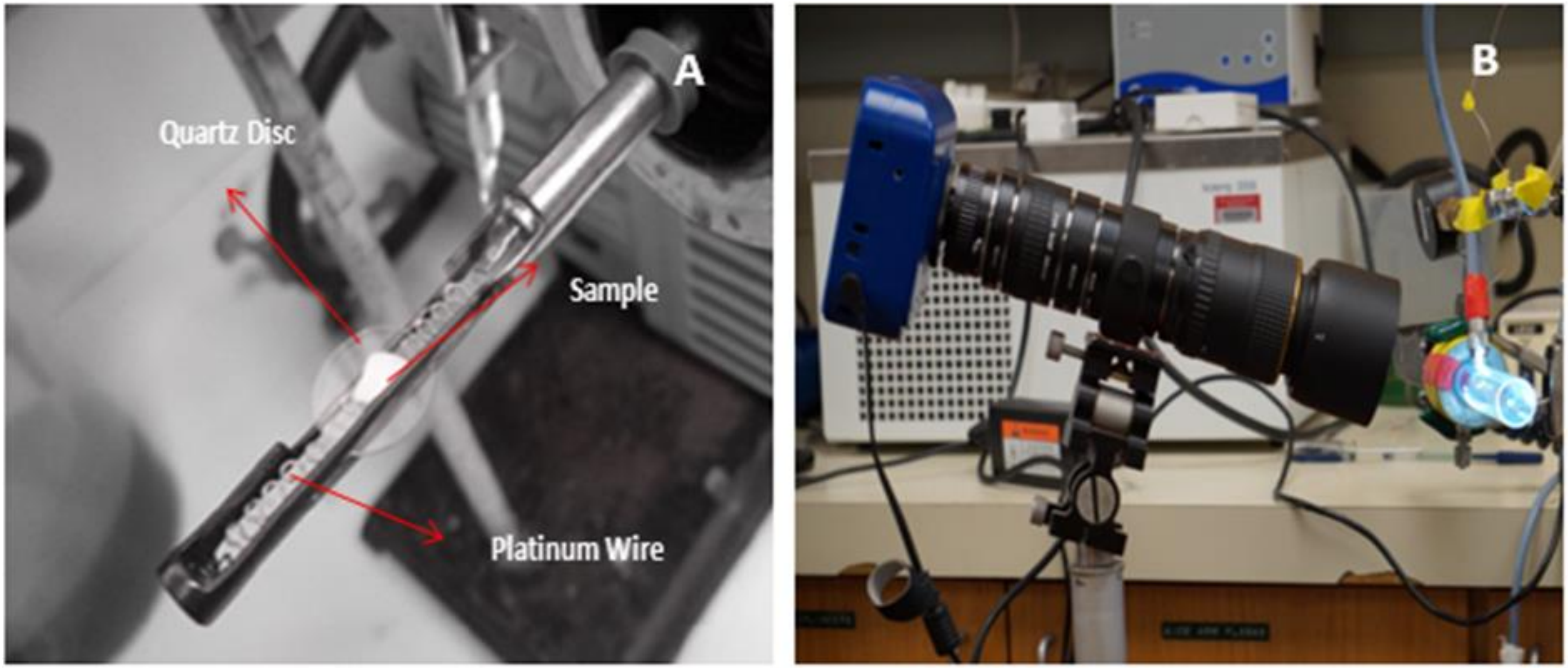
LIGNIN OLIGOMERIC PRODUCTS

Thermal Ejection

Objective:

- **To better understand the mechanisms of thermal ejection of lignin.**

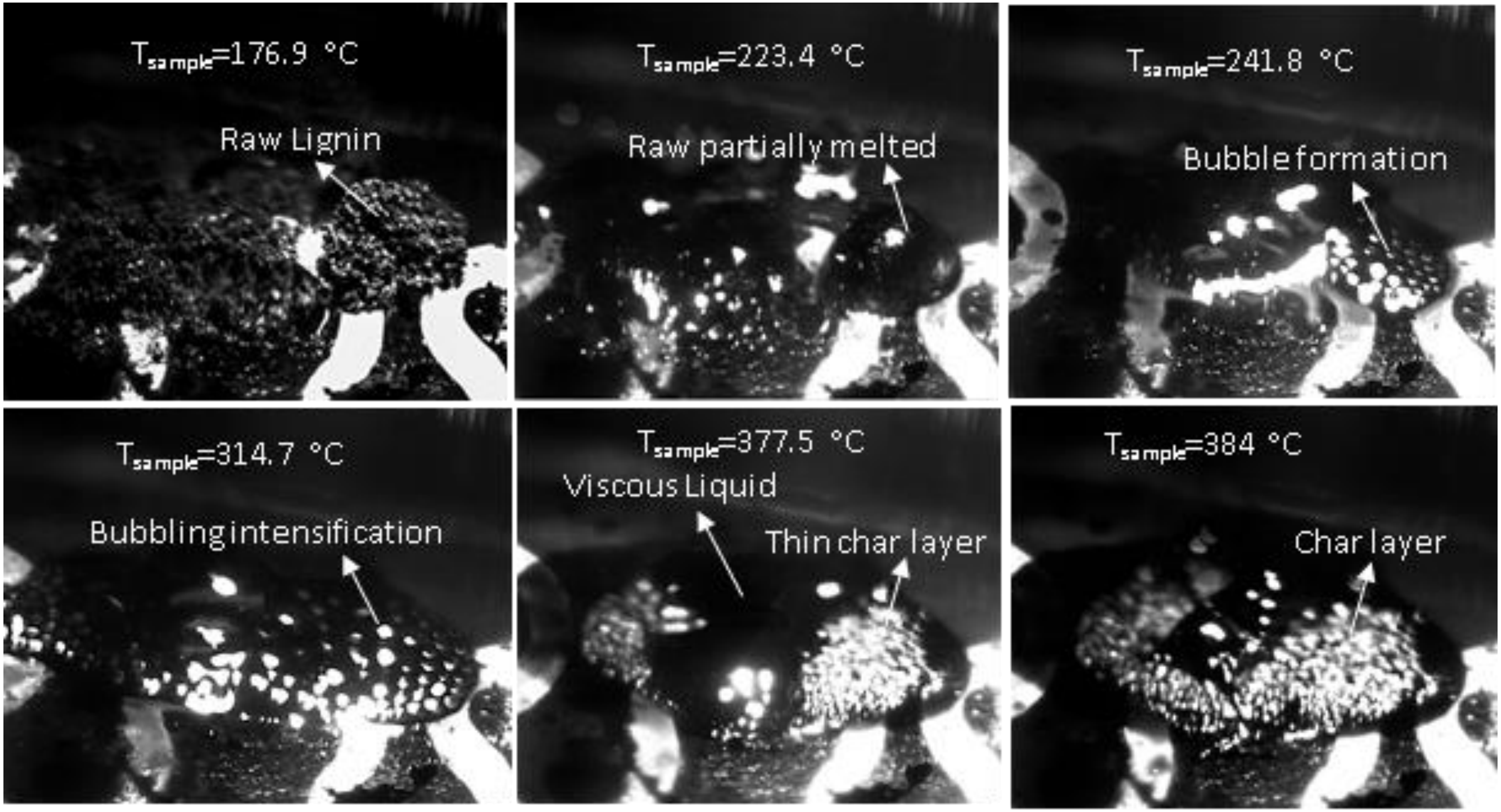




Montoya J, Pecha B, Chejne-Janna F, Garcia-Perez M: Micro-Explosion of Liquid intermediates During the Fast Pyrolysis of Sucrose and organosolv Lignin. Paper Accepted in the Journal of Analytical and Applied Pyrolysis 2016.

LIGNIN OLIGOMERIC PRODUCTS

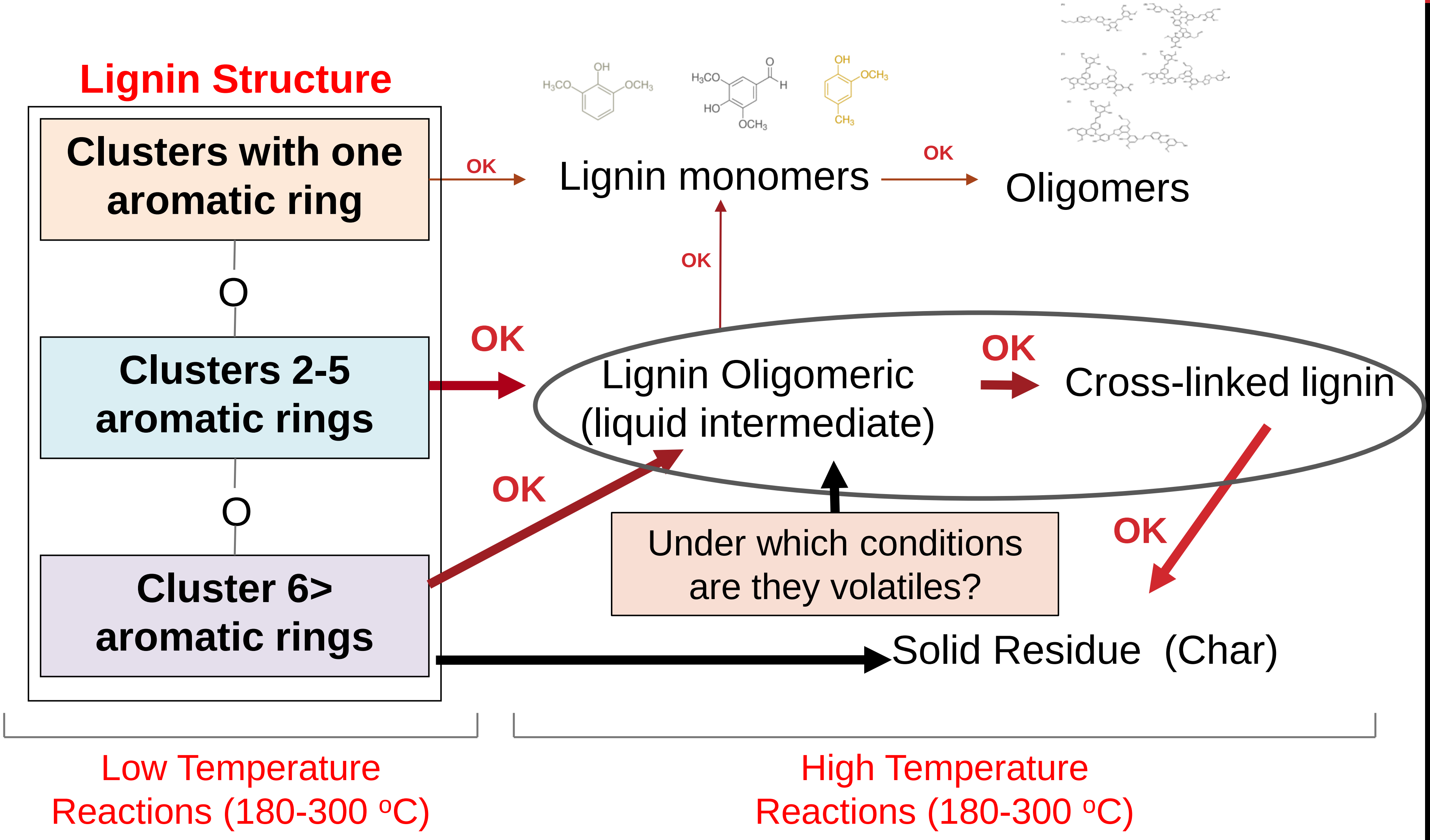
Fast Speed Camera Pictures



Montoya J, Pecha B, Chejne-Janna F, Garcia-Perez M: Micro-Explosion of Liquid intermediates During the Fast Pyrolysis of Sucrose and organosolv Lignin. Journal of Analytical and Applied Pyrolysis 2016. 122, 106-121

PHYSICAL MODEL

Most of the literature considers that the **lignin monomers** are directly produced from the cracking of ether bonds in clusters with one aromatic ring



Lignin Structure

Clusters with one aromatic ring

O

Clusters 2-5 aromatic rings

O

Cluster 6> aromatic rings

OK

Lignin monomers

OK

Oligomers

OK

OK

Lignin Oligomeric (liquid intermediate)

OK

Cross-linked lignin

OK

Under which conditions are they volatiles?

OK

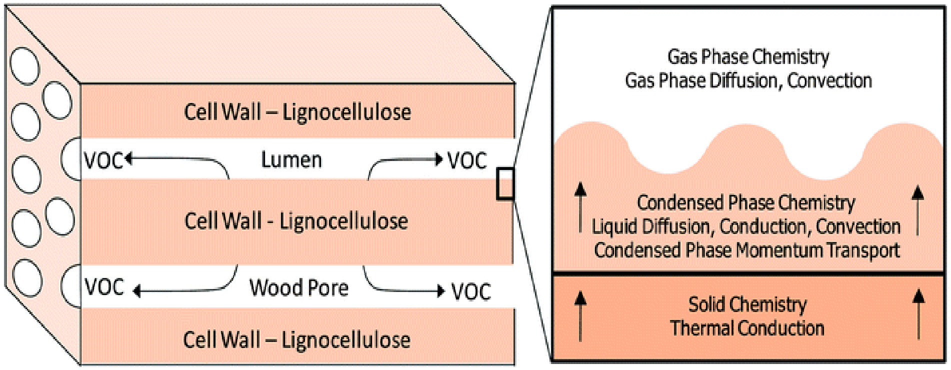
Solid Residue (Char)

Low Temperature Reactions (180-300 ^{o}C)

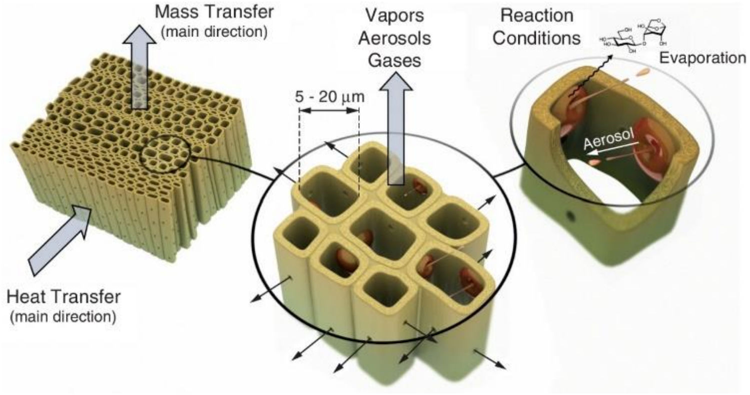
High Temperature Reactions (180-300 ^{o}C)

PHYSICAL MODEL

Dauenhauer model



Kersten/Garcia-Perez model

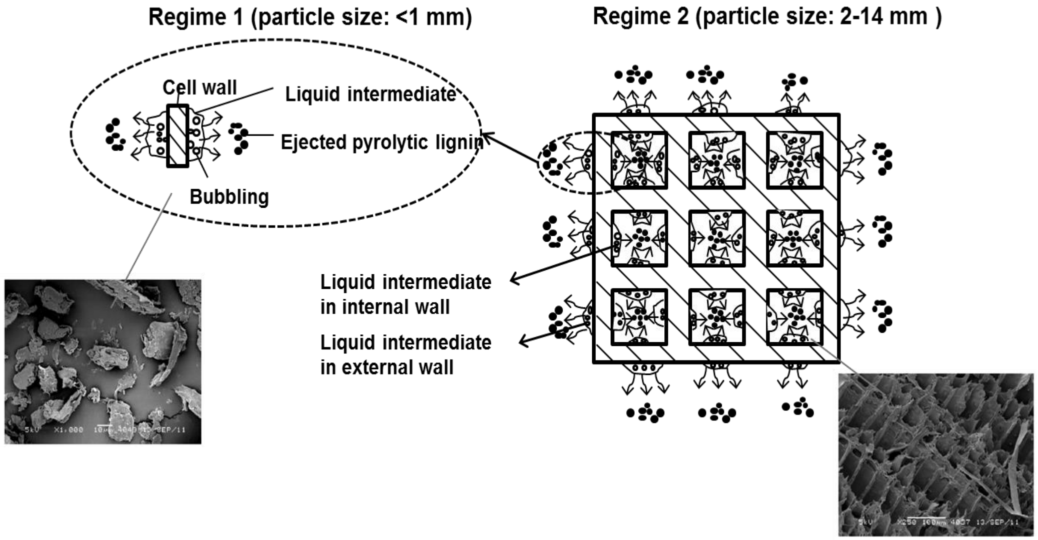


Mettler MS, Vlachos DG, Dauenhauer PJ: Top ten fundamental challenged of biomass pyrolysis for biofuels. Energy & Environmental Science, 2012, 5, 7797

Zhou, S., Garcia-Perez, M., Pecha, B., McDonald, A. G., & Westerhof, R. J. (2014). Effect of particle size on the composition of lignin derived oligomers obtained by fast pyrolysis of beech wood. *Fuel*, *125*, 15-19.

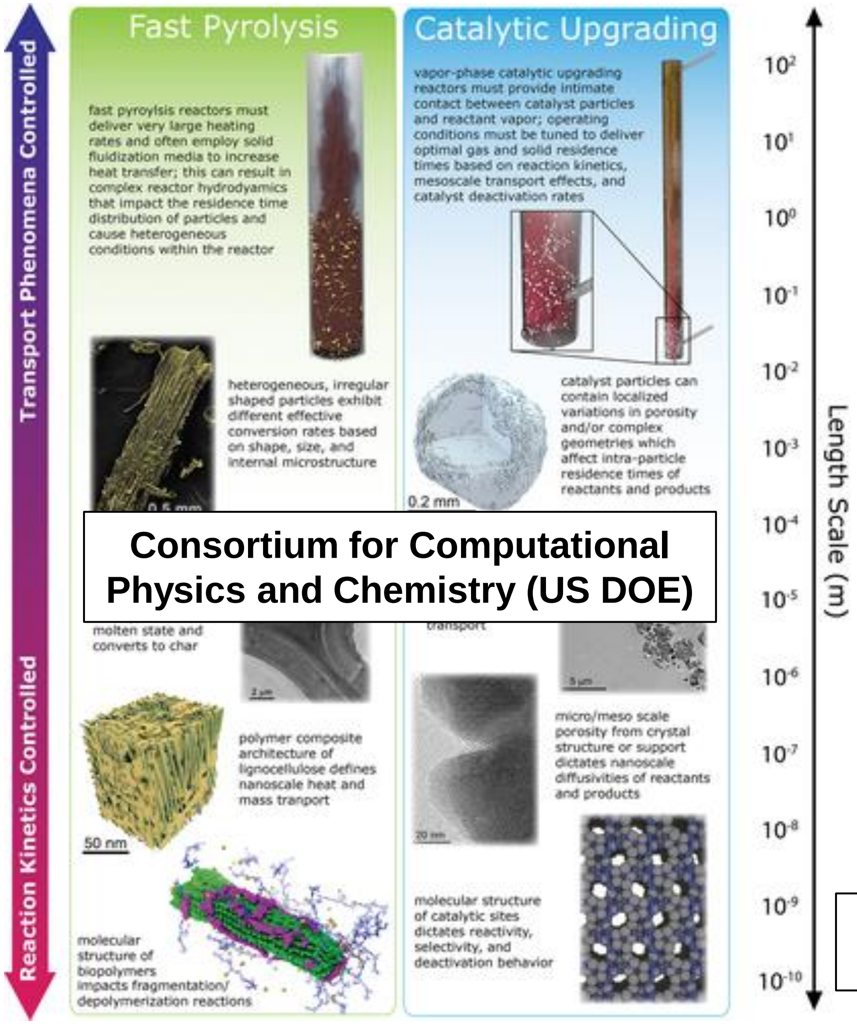
Westerhof, R. J. M., Nygard, H. S., Van Swaaij, W. P. M., Kersten, S. R. A., & Brilman, D. W. F. (2012). Effect of particle geometry and microstructure on fast pyrolysis of beech wood. *Energy & fuels*, *26*(4), 2274-2280.

Kersten S, Garcia-Perez M: Recent developments in fast pyrolysis of lingo-cellulosic materials. Current Opinion in Biotechnology, 2013, 24, 414-420



Progress in Multiscale Modeling and Micro-kinetics

MULTI-SCALE NATURE OF PYROLYSIS REACTOR MODELLING



fast pyroylsis reactors must deliver very large heating rates and often employ solid fluidization media to increase heat transfer; this can result in complex reactor hydrodyamics that impact the residence time distribution of particles and cause heterogeneous conditions within the reactor

heterogeneous, irregular shaped particles exhibit different effective conversion rates based on shape, size, and internal microstructure

molten state and converts to char

polymer composite architecture of lignocellulose defines nanoscale heat and mass tranport

molecular structure of biopolymers impacts fragmentation/ depolymerization reactions

vapor-phase catalytic upgrading reactors must provide intimate contact between catalyst particles and reactant vapor; operating conditions must be tuned to deliver optimal gas and solid residence times based on reaction kinetics, mesoscale transport effects, and catalyst deactivation rates

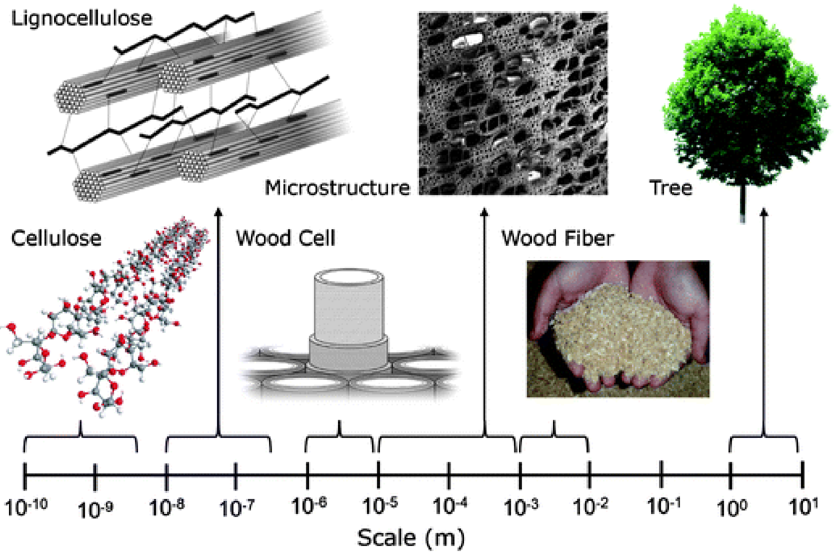
catalyst particles can contain localized variations in porosity and/or complex geometries which affect intra-particle residence times of reactants and products

transport

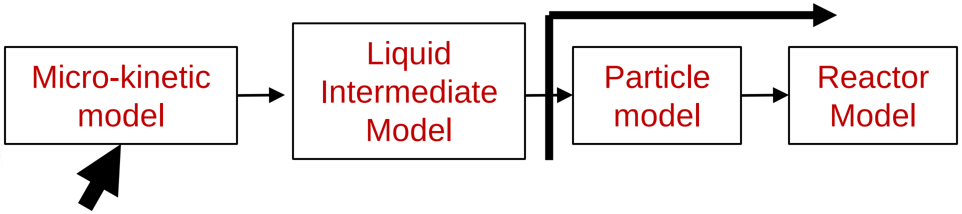
micro/meso scale porosity from crystal structure or support dictates nanoscale diffusivities of reactants and products

molecular structure of catalytic sites dictates reactivity, selectivity, and deactivation behavior

Consortium for Computational Physics and Chemistry (US DOE)



Models at different scales need to be developed in such a way that they exchange information in suitable formats.



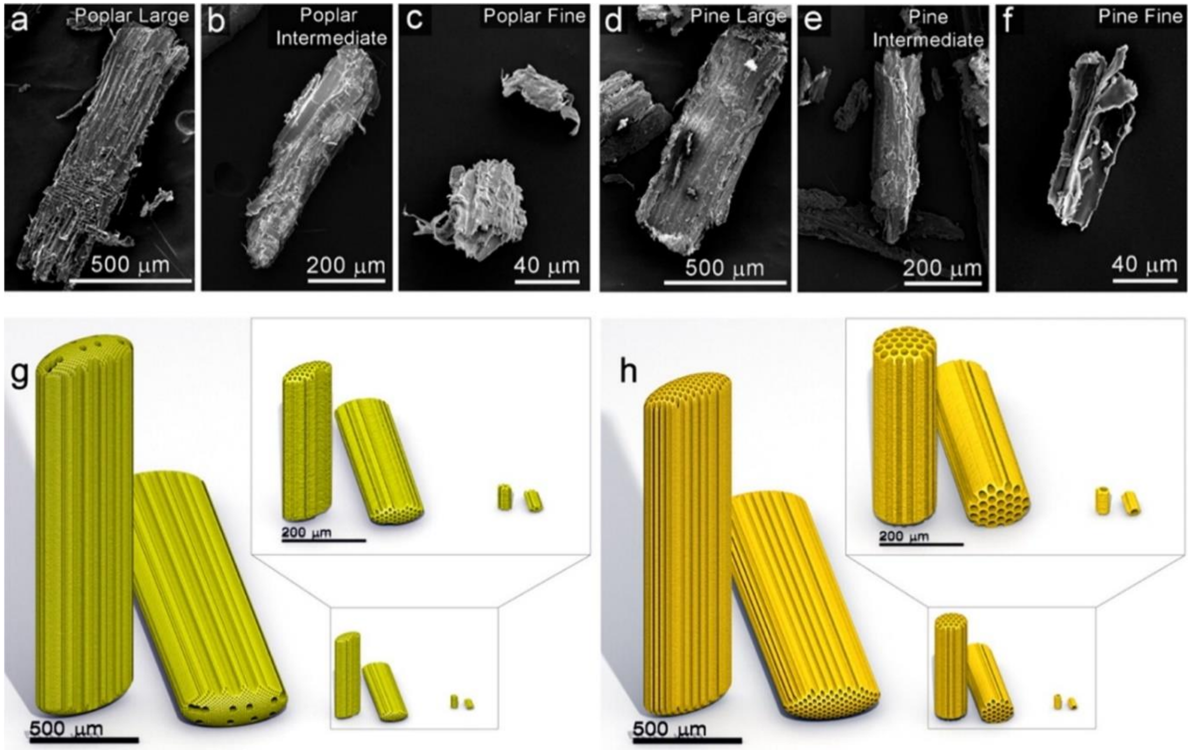
Micro-kinetic model → Liquid Intermediate Model → Particle model → Reactor Model

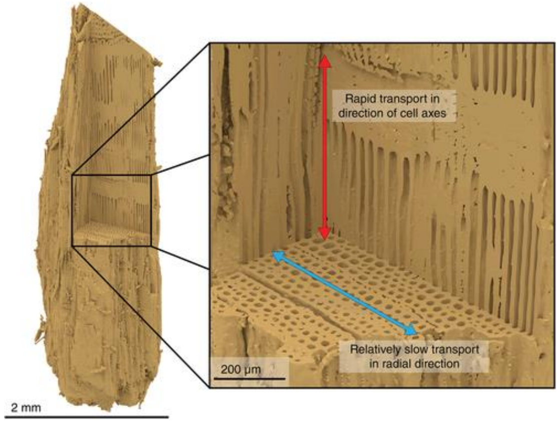
Ciesielski PN, Pecha MB, Bharadwaj VS, Mukarakate C, Leong GJ, Kappas B, Corwley MF, Kim S, Foust TD, Nimlos MR: Advancing catalytic fast pyrolysis thorugh integrated multiscale modeling and experimentation: Challenges, progresses and perspectives. WIRES Energy Environ 2018, 7, e297

Mettler MS, Vlachos DG, Dauenhauer PJ: Top ten fundamental challenged of biomass pyrolysis for biofuels. Energy & Environmental Science, 2012, 5, 7797

MULTI-SCALE NATURE OF PYROLYSIS REACTOR MODELLING

NREL Realistic Model of Biomass Particle



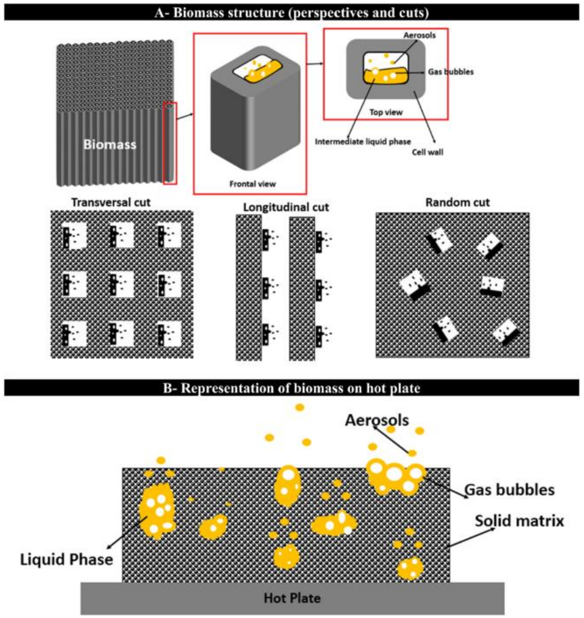


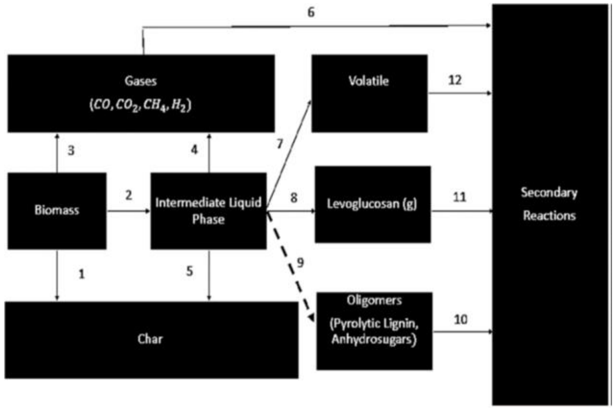
Ciensielski PN, Crowley MF, Nimlos MR, Sanders AW, Wiggins GM, Robichaud D, Donohoe B, Foust TD: Biomass Particle Models with Realistic Morphology and Resolved Microstructure for Simulations of Intraparticle Transport Phenomena. Energy Fuels, 2015, 29 (1), 242-254

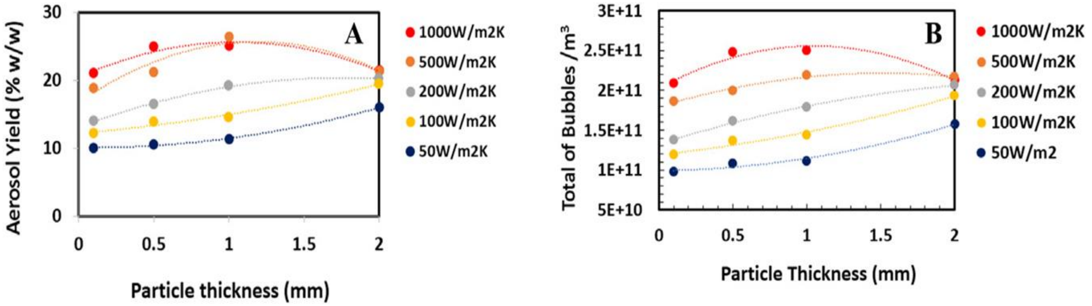
Ciesielski PN, Pecha BM, Bharadwaj VS, Mukarakate C, Leong JG, Kappes B, Crowley M, Kim S, Foust TD, Nimlos MR: Advancing catalytic fast pyrolysis through integrated multiscale modeling and experimentation: Challenges, progress and perspectives. WIRES Energy Environ, 2018, 7:e297

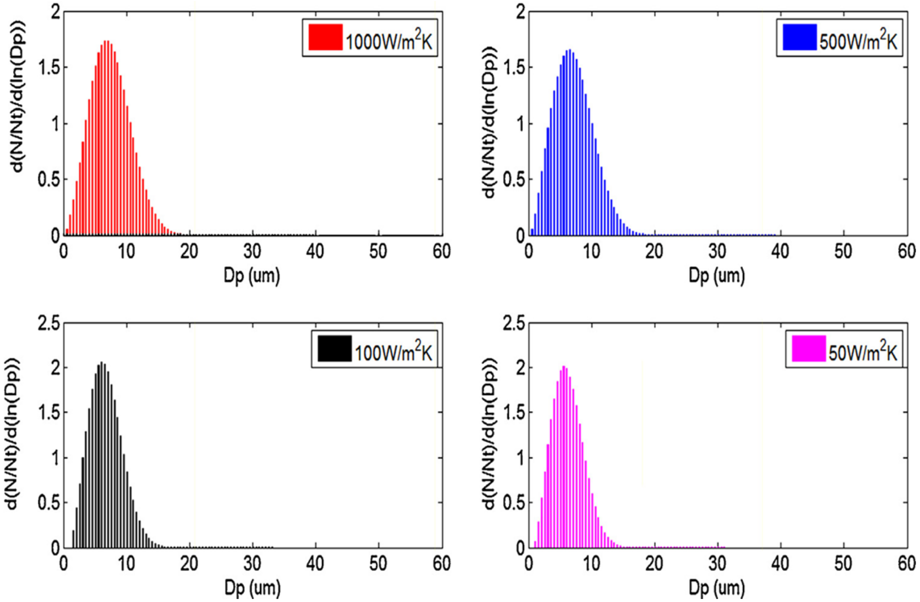
THERMAL EJECTION

First model that explicitly considers the role of liquid intermediates (Montoya et al 2017)





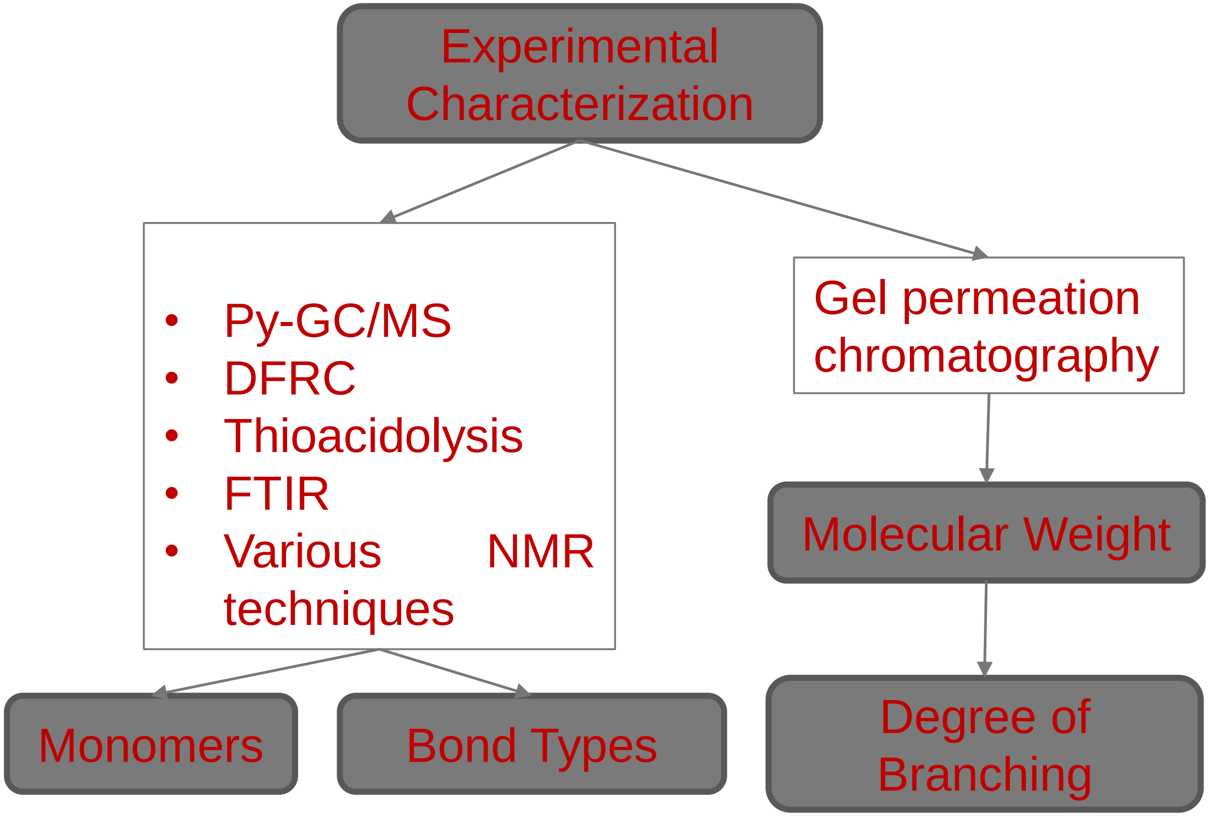




Montoya J, Pecha B, Chejne FJ, Garcia-Perez M: Single particlicle model for biomass pyrolysis with bubble formation dynamics inside the liquid intermediate and its contribution to aerosols formation by thermal ejection. Journal of Anlytical and Applied Pyrolysis, 124, 2017, 204-218

LIGNIN STRUCTURAL REPRESENTATION

BROADBELT’S METHOD



Experimental Characterization

- Py-GC/MS
- DFRC
- Thioacidolysis
- FTIR
- Various NMR techniques

Gel permeation chromatography

Molecular Weight

Monomers

Bond Types

Degree of Branching

Experimental data used directly as inputs into computational structure model

Use stochastic method for generating “libraries” of lignin structures (Yanez et al 2016, Dellon et al 2017)

No such thing as “one” lignin structure

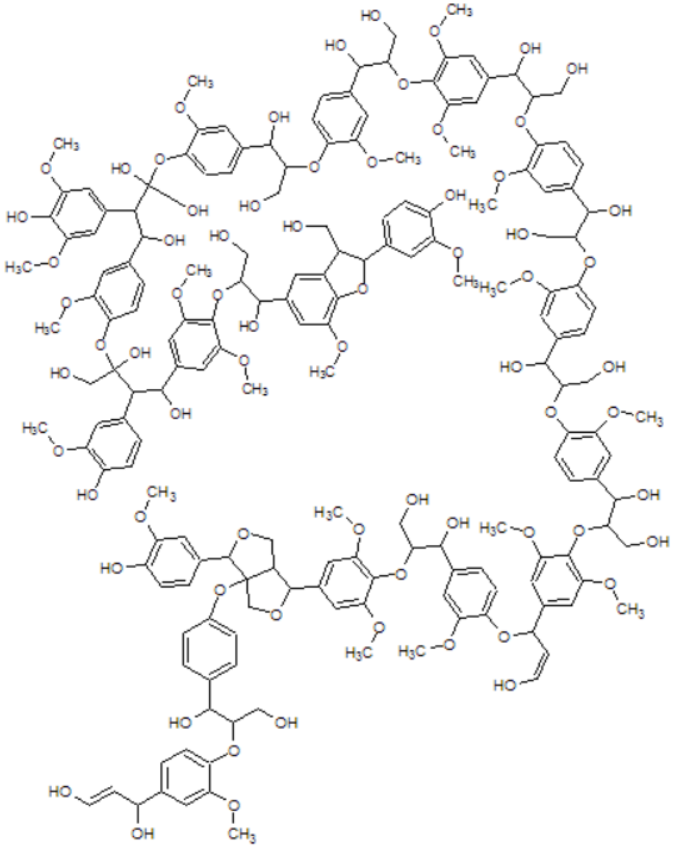
- Better approach is to build ~10^3-10^6 molecular representations

Yanez, et al. *Energy Fuels* (2016), 30, 5835-5845.
Dellon, et al. *Energy Fuels* (2017), 31, 8263-8274.

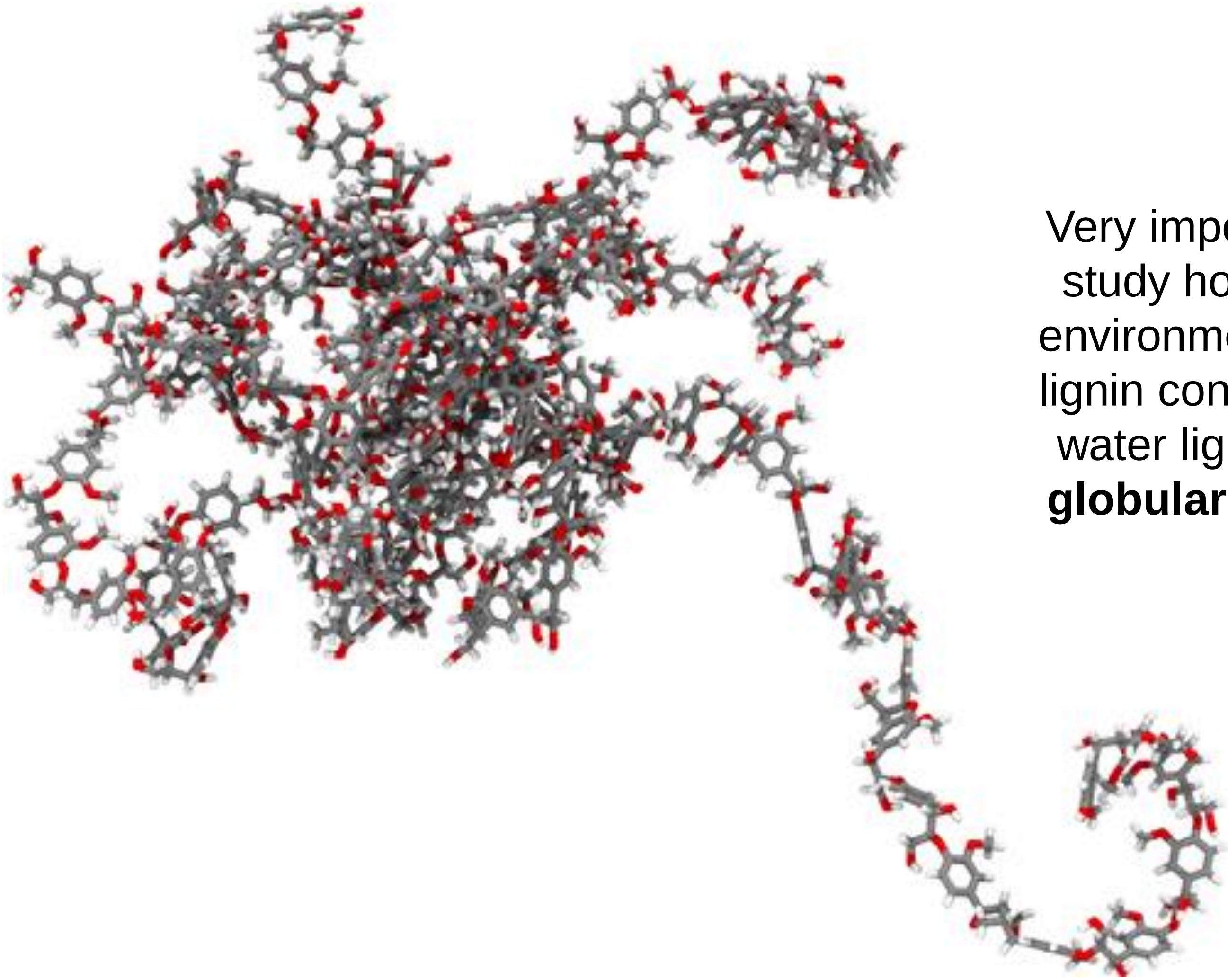
LIGNIN STRUCTURAL REPRESENTATION

STOCHASTIC STRUCTURE MODELING

Parameter	Target (%)	Computed
H monomer	2	1.91
G monomer	63	62.26
S monomer	35	35.82
M_n	3690	4258.95
M_w	5510	5401.10
β-O-4	60	60.01
α-O-4	5	5.12
β-1	15	15.16
β-β	10	10.22
β-5	6	5.99
4-O-5	2	2.19
5-5	2	1.32



LIGNIN STRUCTURAL REPRESENTATION

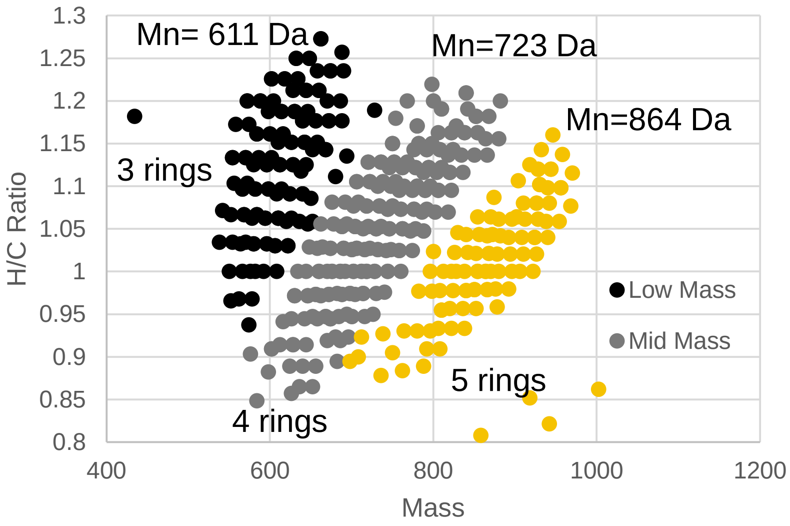


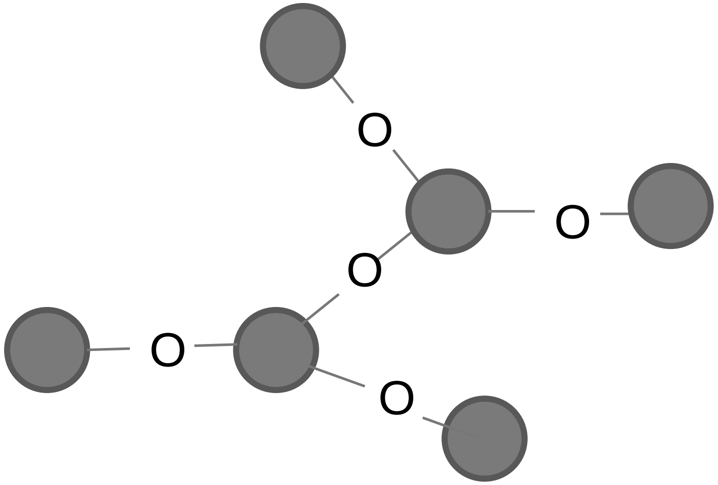
Very important tool to study how chemical environment influence lignin configuration. In water lignin adopted **globular structures**.

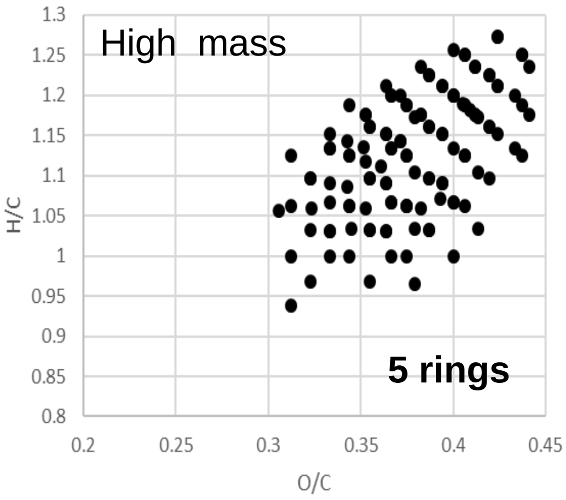
Vermaas JV, Dellon LD, Broadbelt LJ, Beckham GT, Crowled MF: Automated Transformation of Lignin Topologies into Atomic Structures with LigninBuilder. ACS Sustainable Chemistry & engineering, 2019, 7, 3, 3443-3453

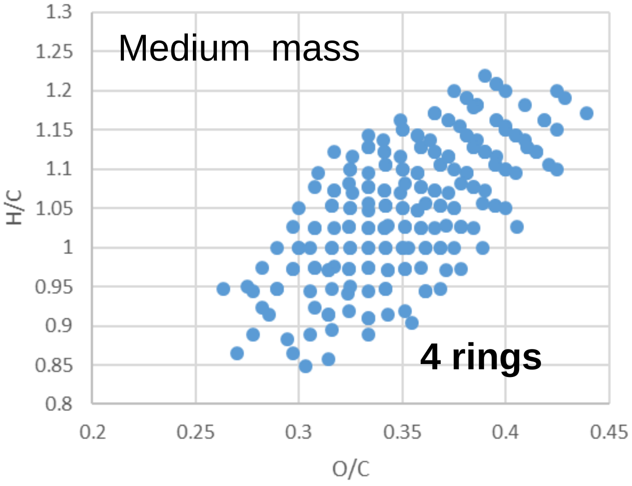
LIGNIN STRUCTURE

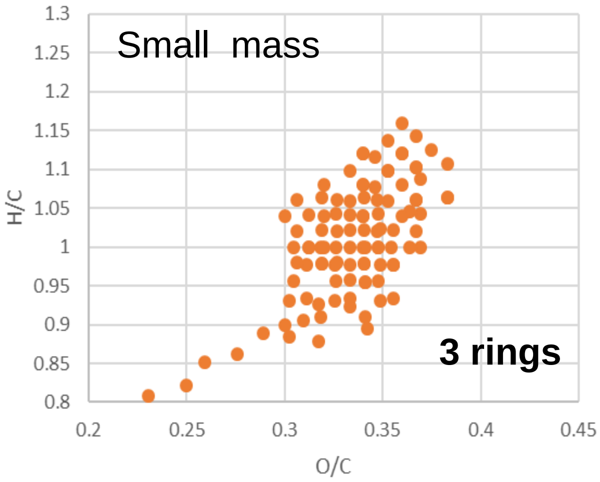
Lignin: continuous vs. cluster structure (MALDI-ICR-MS) (**On going work with Anthony Dufour, French National Center for Scientific Research**)



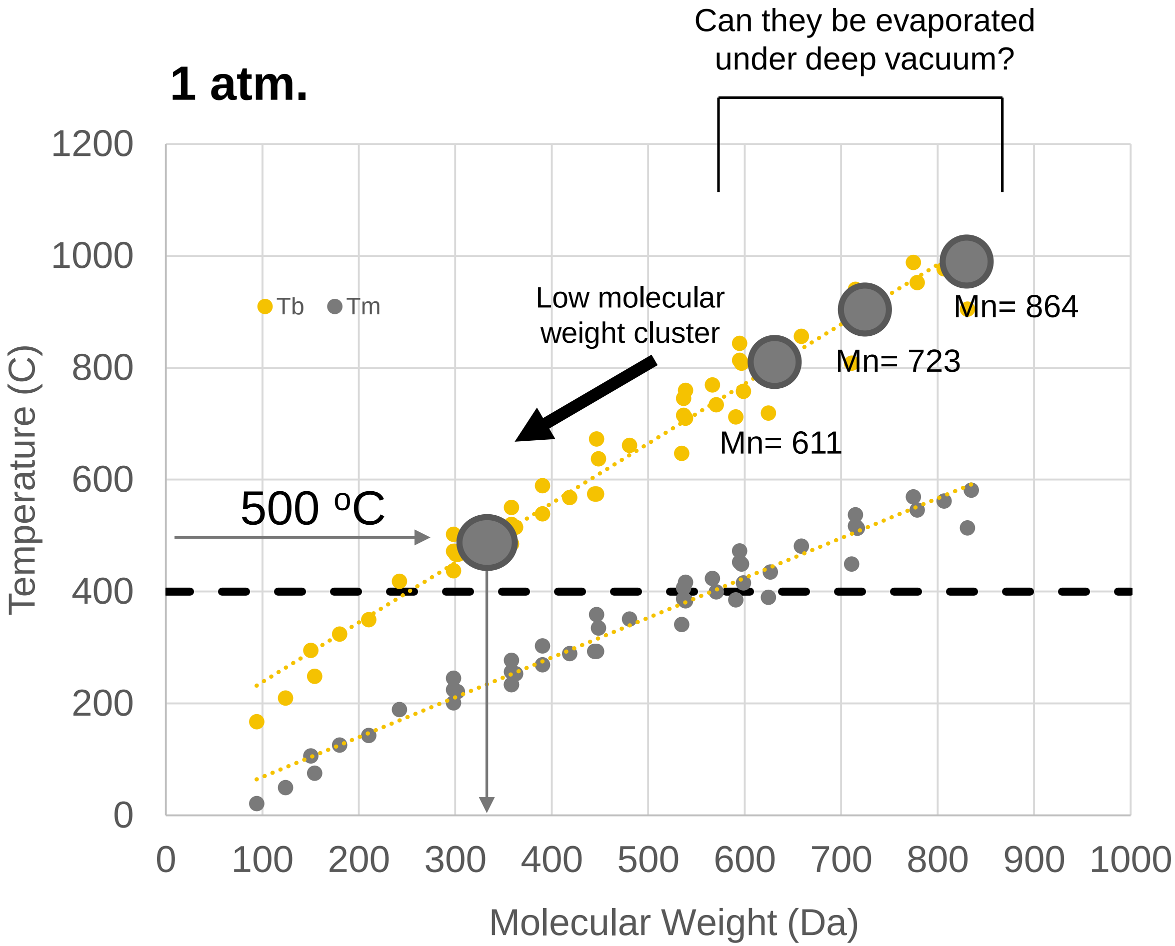


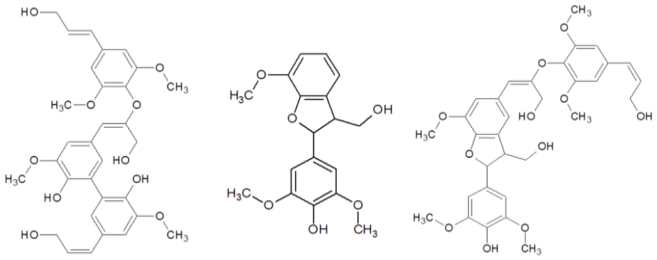






LIGNIN EVAPORATION





Thermodynamic Properties of Lignin Fragments (Group Contribution Theory)

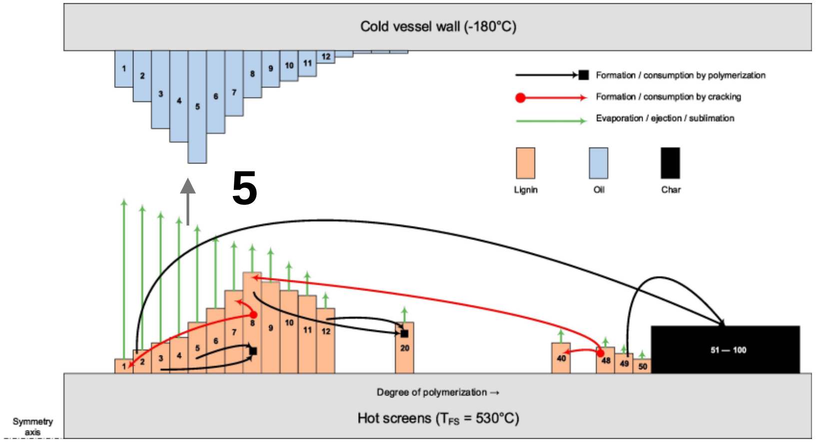
In pyrolysis the clusters need to shrink (Fundamental difference between pyrolysis and solvolysis)

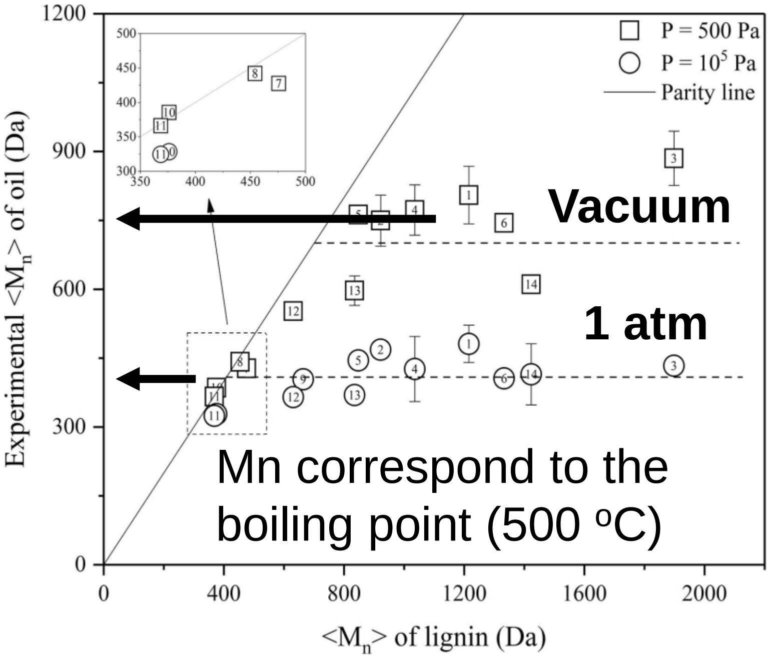
Terrell E, Broadbelt L, Dufour A, Le Brech Y, Garcia-Perez M: Calculation of Boiling and melting Thermodynamic Parameters for Lignin Pyrolysis Decomposition Fragments using Group Contribution. Paper in preparation, To be Submitted (2019)

LIGNIN OLIGOMERIC PRODUCTS

Is lignin pyrolysis controlled
by evaporation of oligomers?

This result suggest that perhaps it is
posible to evaporate the clusters
under vacuum

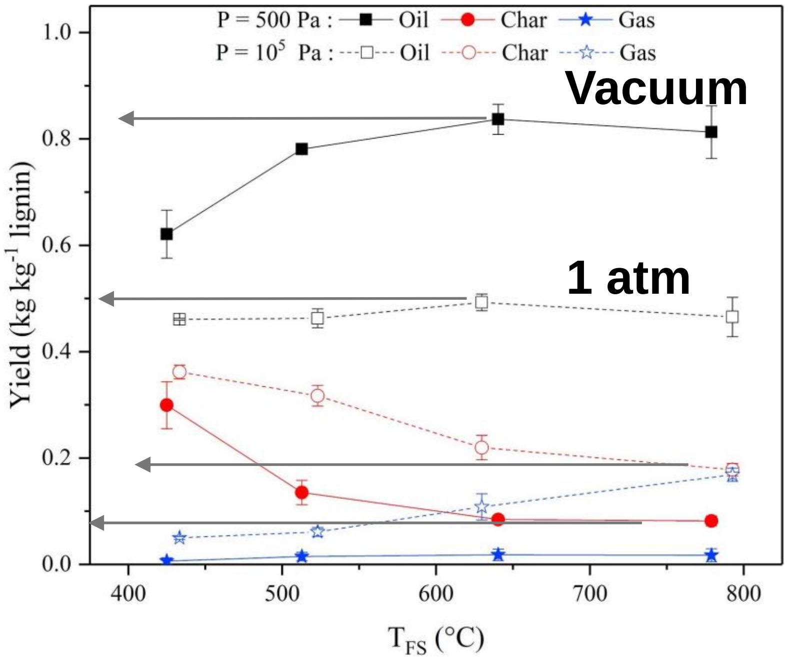




Vacuum

1 atm

Mn correspond to the boiling point (500 ºC)



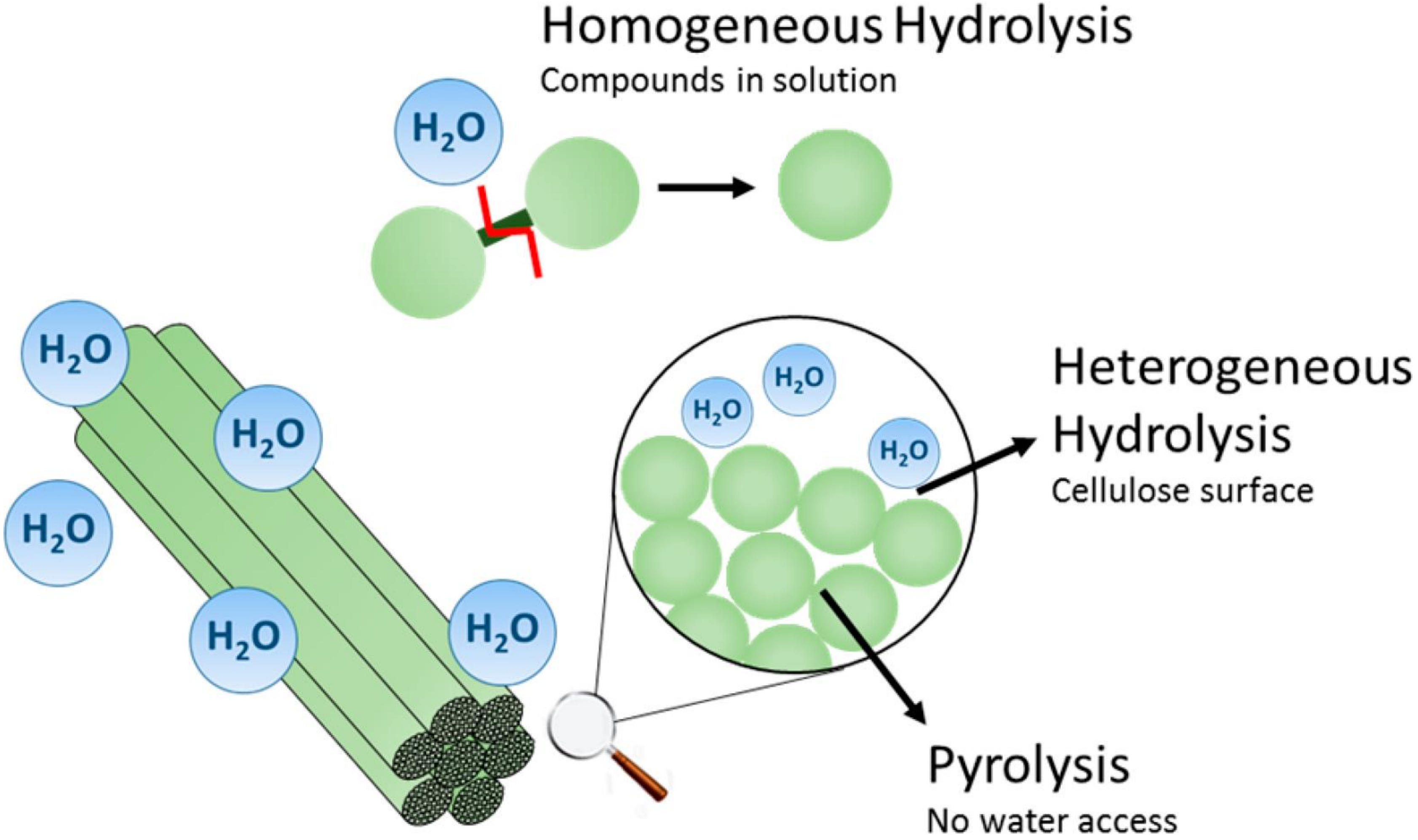
Vacuum

1 atm

Marathe PS, Westerhof RJM, Kersten SRA: Fast Pyrolysis of lignins with dfferent molecular weight: Experiments and modelling. Applied Energy, 236, 2019, 1125-1137

SOLVENT EFFECT

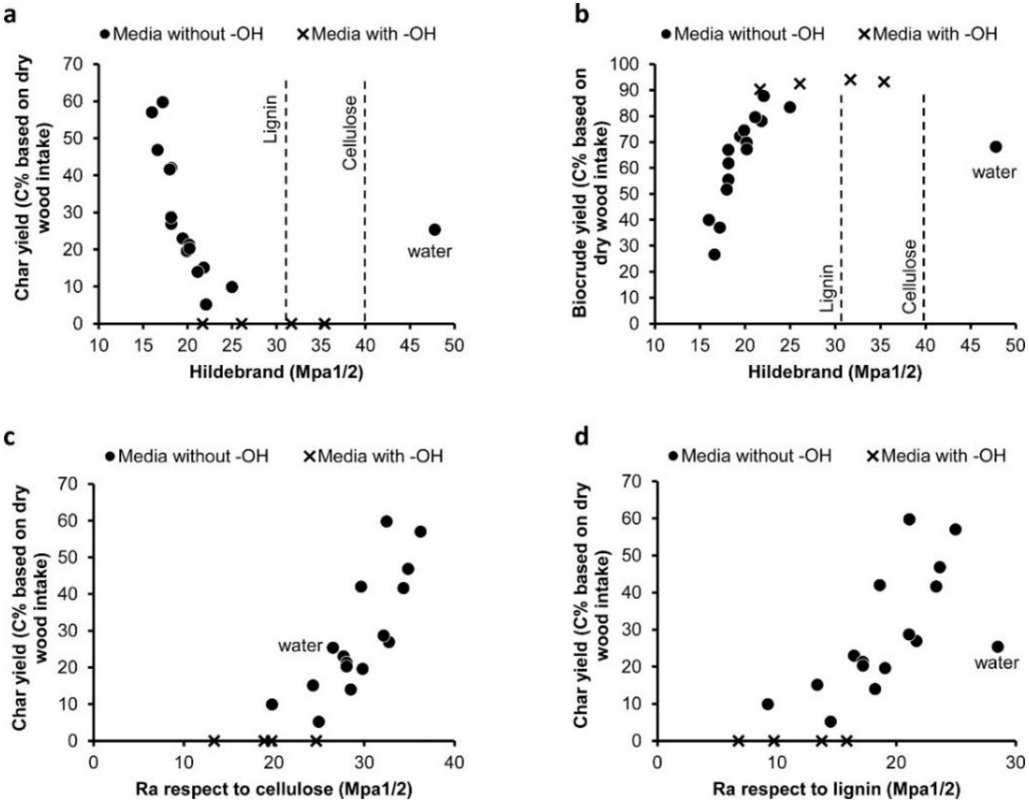
PHYSICAL MODEL DESCRIBING CELLULOSE HYDROTHERMAL LIQUEFACTION (Dr. Dufour's Group)



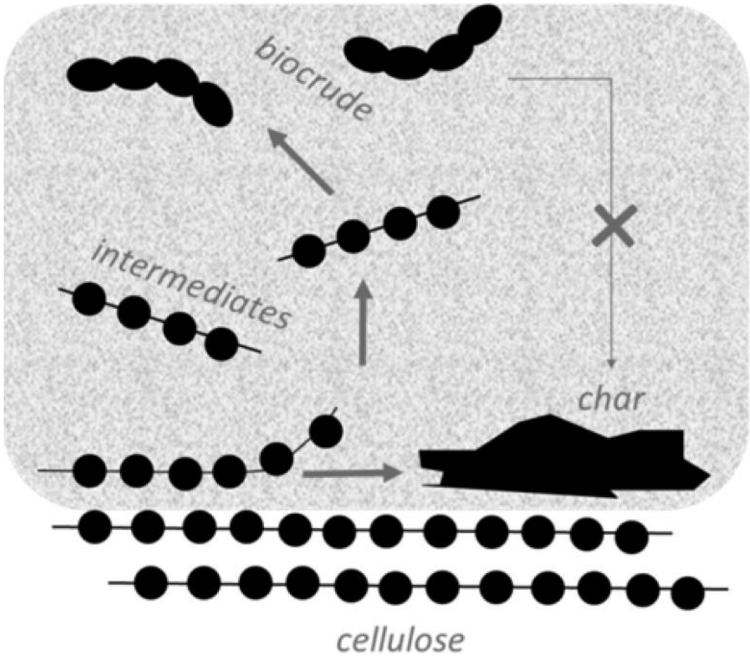
Buendia-Kandia F, Mauviel G, Guedon E, Randags E, Petijean D, Dufour A: Decomposition of Cellulose in hot-compressed water: Detailed Analysis of the Products and Effect of Operating Conditions. Energy Fuels, 2018, 4127-4138

SOLVENT EFFECT

Twente University



Liquefaction is strongly affected by the choice of the **liquefaction solvent**. The solvent appeared to influence the liquefaction through **interaction with early reaction products**. Char was formed by the **degradation of early liquefaction products (insoluble liquid intermediate).**

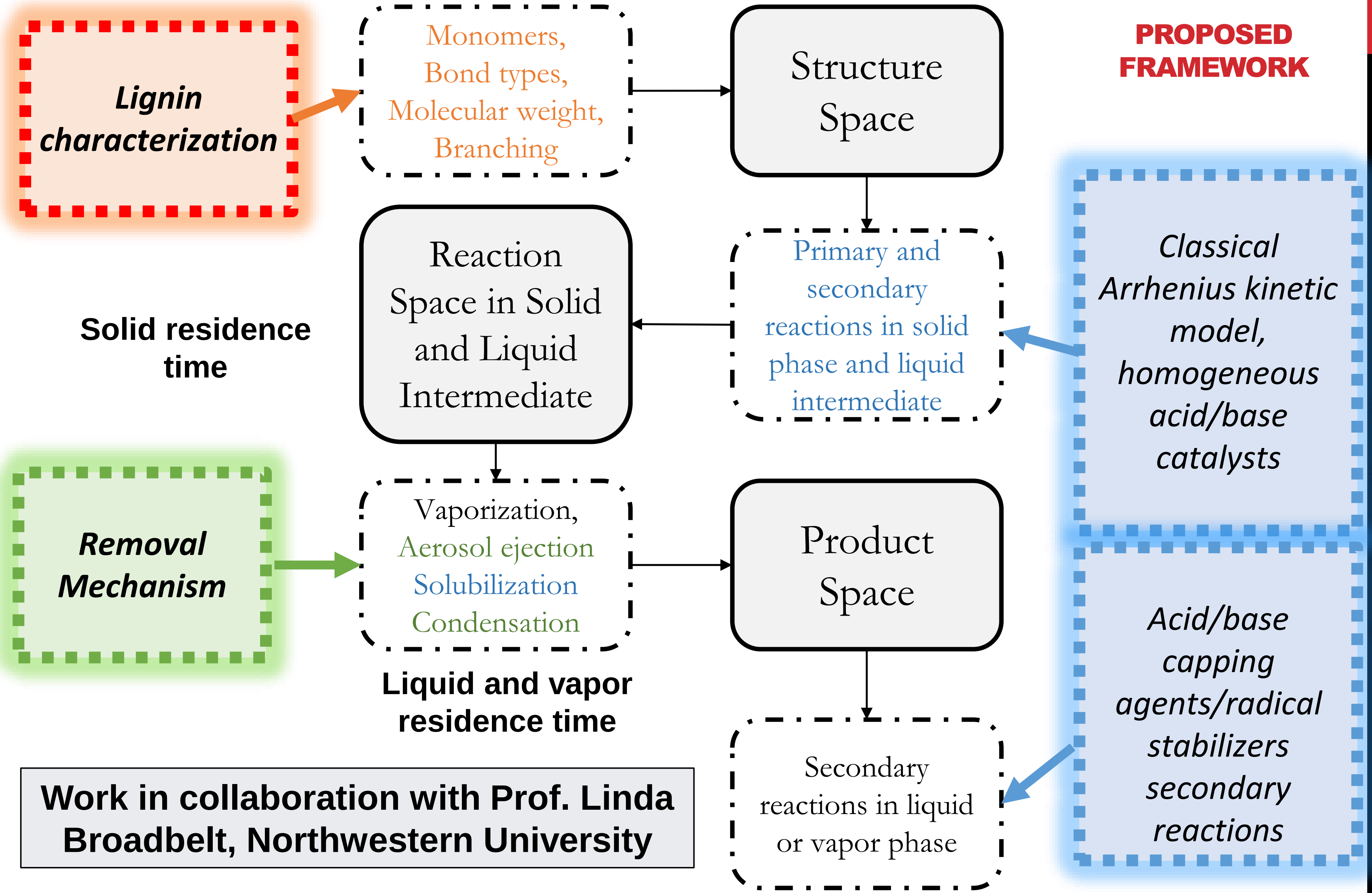


Solubility of early liquid intermediate (removal mechanism) seems to be critical for solvolysis and hydrothermal liquefaction

Castellvi Barnes M, Oltvoort J, Kersten SRA, Lange J-P: Wood Liquefaction: Role of Solvent. Ind. Eng. Chem. Res. **2017**, 56, 635-644

MICRO-KINETICS OF LIGNIN THERMOCHEMICAL CONVERSION

PROPOSED FRAMEWORK



Lignin characterization

Monomers,
Bond types,
Molecular weight,
Branching

Structure Space

Primary and secondary reactions in solid phase and liquid intermediate

Classical Arrhenius kinetic model, homogeneous acid/base catalysts

Reaction Space in Solid and Liquid Intermediate

Solid residence time

Removal Mechanism

Vaporization,
Aerosol ejection
Solubilization
Condensation

Liquid and vapor residence time

Product Space

Secondary reactions in liquid or vapor phase

Acid/base capping agents/radical stabilizers secondary reactions

Work in collaboration with Prof. Linda Broadbelt, Northwestern University

SUMMARY AND OUTLOOK

Micro-kinetic modeling can significantly advance opportunities for lignin utilization

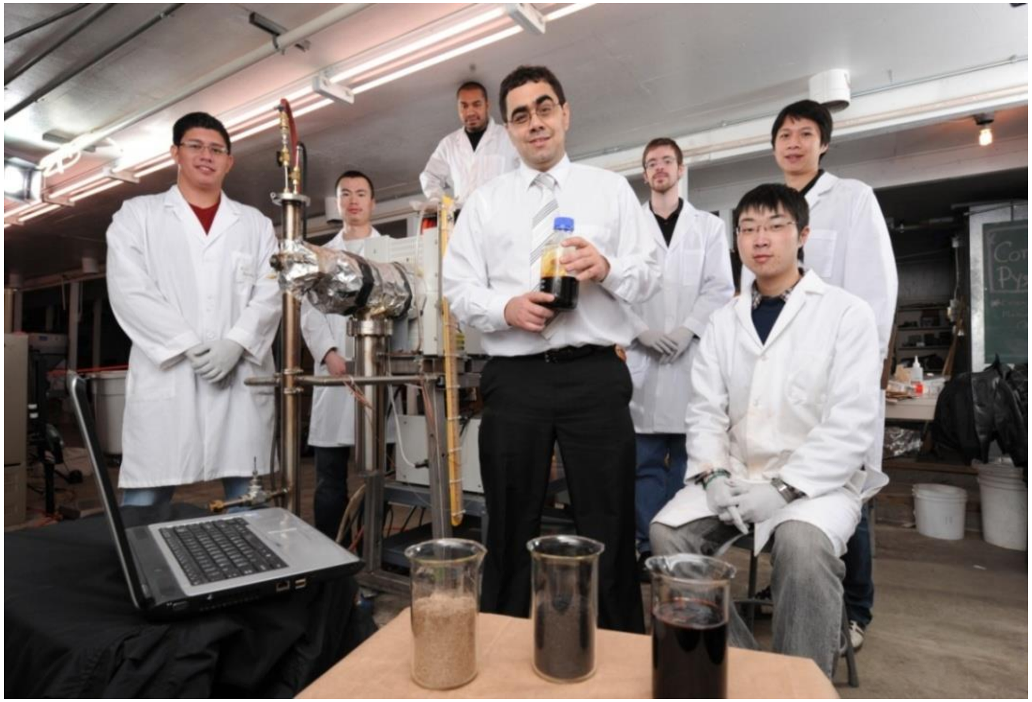
Model based first on stochastic structure building that relies directly on experimental data inputs

Chemical kinetics alone for lignin depolymerization are relatively well-understood

Great opportunities for incorporation of thermo-physical and non-reactive processes, like evaporation, aerosol ejection and the effect of solvent

Need to keep developing new experimental and analytical techniques – especially reaction visualization and high-resolution mass spec!

ACKNOWLEDGEMENT



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WASHINGTON STATE DEPARTMENT OF ECOLOGY
U.S. DEPARTMENT OF ENERGY

QUESTIONS?