Biomass pyrolysis: advanced experiments and modeling

PhD position available at CNRS Nancy, France
In collaboration with USA partners

CNRS, Université de Lorraine, Nancy, France
Washington State University, Pullman, USA

Contact: anthony.dufour@univ-lorraine.fr

Sept. or Oct. 2022 to Sept. or Oct. 2025

Summary

Biomass pyrolysis is a key topic for carbon sequestration, green energy production and biorefinery. This project deals with advanced experiments and modeling in order to better understand biomass pyrolysis. We will do laser heating pyrolysis. Biomass pyrolysis produces volatile compounds and char. The volatiles will be analyzed by advanced mass spectrometry. The char will be characterized by various spectroscopic and imaging methods. The kinetics of surrogate macromolecules pyrolysis will be modeled by lumped models. Heat and mass transfers at the cell-wall and particle scales will be modeled in collaboration with our US partners (Prof. M. Garcia-Perez).

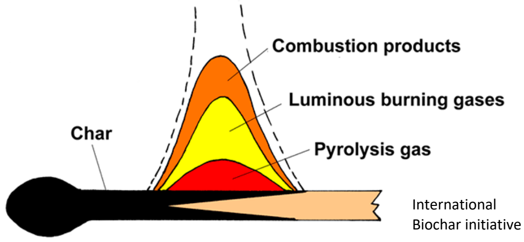
Context

Biomass use could reach 108 exajoules (EJ) worldwide by 2030 (double the current level) and could account for 20% of total primary energy supply [1]. Only 48% of the estimated potential of solid biomass in the EU-27 is currently used [2]. Wood chips (from forest residues), agricultural wastes and fast growing crops represent the highest potential [2]. These lignocellulosic biomasses can be converted to heat, electricity, biofuels and chemicals by various processes, such as combustion, gasification or pyrolysis.

Biomass combustion leads to important health and environmental impacts.
A third of the world's population – 2.5 billion people – still rely on the traditional use of solid biomass (like wood) to cook their meals in inefficient stoves. Inefficient open fires stoves particularly expose women and children with toxic indoor smoke. Household air pollution is linked to around 2.5 million premature deaths annually [3]. Stoves and forest fires emit organic species and aerosols in the atmosphere which play important roles in atmospheric chemistry and global warming.[4]

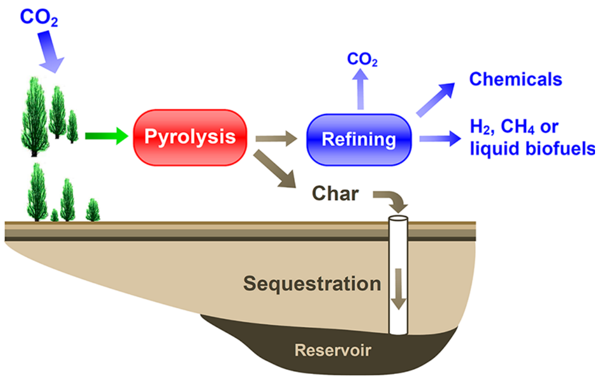
Why it is important to study biomass pyrolysis:

1) Biomass pyrolysis is a key phenomenon during combustion in cooking stove, industrial reactors and forest fires.



During combustion, biomass is heated, dried and the macromolecules (cellulose, lignin, etc.) undergo bond breaking ("pyrolysis") to form volatiles (permanent gas and tar) and char. Volatiles and char are then oxidised by air. The oxidation of pyrolysis products is not complete in forest fires or inefficient stoves. Pyrolysis is a source of pollutants formation (CO, aromatics, "brown carbon" in organic aerosol, etc.). Therefore, it is important to better understand pyrolysis mechanisms in order to reduce the health and environmental impact of biomass combustion.

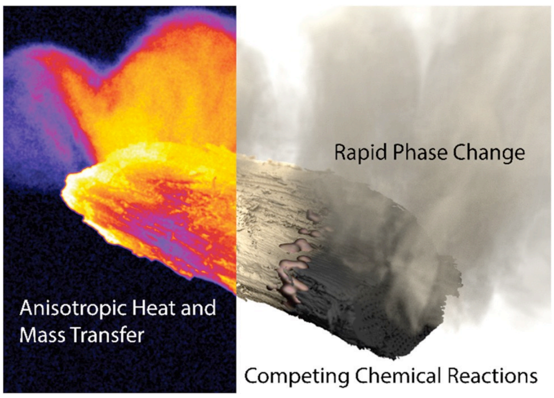
2) Pyrolysis is an important process for carbon sequestration and biofuels production



Net negative emission routes are required to limit anthropogenic climate change. The total potential for negative emissions would be in the order of 10 $GtCO_2$/year for bioenergy with carbon capture and storage [5]. Pyrolysis is a fundamental mechanism occurring during combustion but it is also a process itself if biomass is heated in an inert or anoxic atmosphere. Pyrolysis-based biorefineries offer an interesting approach for carbon storage and biofuels production. It can produce liquids (bio-oil) rich in various chemicals and a biochar (or "charcoal"). Biochar can be sequestered by land application or by geological sequestration thus creating recoverable "bio-mines" (in reservoir) for future generations [6]. Pyrolysis-based refineries have been developed to produce char and dozens of chemicals since the early twentieth century (like in Premery, France). This industry then declined with the development of fossil fuels (oil, coal and gas). Biomass pyrolysis currently regains considerable interest to produce biofuels, chemicals and for carbon sequestration.

State of the art

The current state of knowledge about the fundamentals of biomass pyrolysis have been extensively reviewed [7–10]. The main mechanisms are displayed on the following figure (taken from ref.[9]).



1) Heat transfers

First of all, heat is brought by the reactor (or fire) to the external surface of the wood particle. Wood presents a poor thermal conductivity and an anisotropic structure. The conductivity parallel to the fiber is approximately twice the conductivity in perpendicular direction [11]. An important thermal gradient can occur inside the particles depending on particle size and heat flux density brought to the particles [12].

2) Phase change

Upon heating, the macromolecules present in wood cells are converted into an intermediate liquid, like a "hot caramel", through glass phase transition and bond breaking (depolymerisation) [13]. This intermediate liquid can be evaporated (depending on partial pressure of pyrolysis gas) or converted to char, a cross-linked carbonaceous solid.

3) Reactions

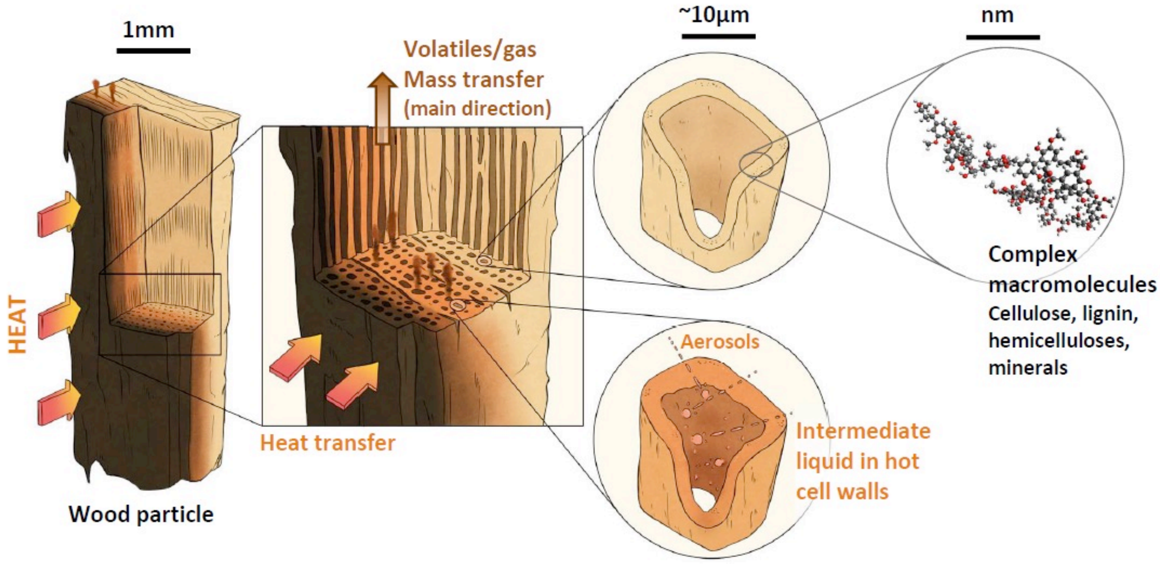
Cellulose, lignin and hemicelluloses present dozens of different chemical moieties which undergo complex reactions between 150 and 600°C such as dehydration, decarbonylation, transglycosylation (to form levoglucosan), demethoxylation, etc. The minerals (K, Na, Ca, etc.) naturally present in biomass interact with organic functional groups and considerably impact pyrolysis reactions. They notably promote cracking reactions and inhibit transglycosylation. Various kinetic models have been proposed but very few intend to model the chemical composition of the products. Broadbelt et al. have proposed stochastic molecular reconstruction and advanced kinetic modeling of lignin pyrolysis [14]. Ranzi et al. [15] have developped the most complete lumped kinetic model, then improved by Anca-Couce et al. [16]. But these advanced models still fail to capture the impact of minerals on the chemical composition of volatiles. The synergies between the macromolecules inside wall cells are also not yet modeled.

4) Mass transfers

Once volatiles are formed inside the "hot caramel", they swell this visco-elastic material and form bubbles which burst and can release liquid aerosols. Aerosols and gas/vapours escape from the particle mainly in the direction of fiber axes. They may also deposit over the cell walls and undergo secondary reactions (at liquid or vapour phase) [9,17].

Main issues to overcome in order to reveal the fundamentals of biomass pyrolysis

The scheme below (edited by CNRS-Nancy for this project, adapted from ref. [9,18]) displays the multiscale nature of wood pyrolysis.



Herein, heat is brought by only one side of the particle in order to highlight the thermal gradient inside the particle and the chemical profile from char to pristine (not converted) wood. In reactor, heat is brought all around the external surface of the particle and is better conducted along the fibers' axe. The first important issue is to assess the anisotropic heat transfer inside wood particles.

To the best of our knowledge, heat transfers at the cell wall level have been yet poorly studied notably during pyrolysis [19,20]. The true temperatures during fast pyrolysis reactions remain unknown. They could be revealed by temperature imaging linked to the real-time analysis of the products. Upon heating, the macromolecules present in the cell walls form an intermediate liquid, like a "hot caramel". The chemistry of this reactive liquid, its conversion and transport are not yet well understood. The bubbling and ejection of liquid droplets which carry heavy products (oligomers) as aerosols is an important phenomena and need deeper work [9,21]. The heat and mass transfers inside this "boiling film" but also its visco-elastic properties should be studied. Furthermore, the macromolecules and minerals form a complex reactive network in the walls with strong interactions. A simple physical mixing of extracted macromolecules (e.g. cellulose with lignin) does not surrogate properly the chemical complexity of the natural network in cell walls. The synergies between macromolecules, minerals and intermediate species in the cell walls are not yet captured by the available kinetic mechanisms.

Research project of this PhD

The program remains very open and it can be adapted depending on the strength and wishes of the best selected candidate. Other international partners may also join the team.

The target of this PhD is to develop advanced well-controlled experiments in order to reveal and model the mechanisms of biomass pyrolysis.
We intend to conduct experiments with a novel laser device (developed at CNRS Nancy) on:

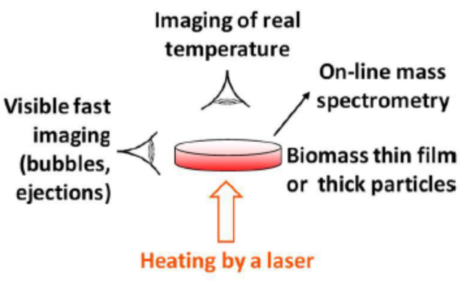
1) Model macromolecules (cellulose, lignines, hemicelluloses);
2) Different particles of real-life biomasses.

The experiments will be conducted at different heat flux densities and pyrolysis time (from 1sec. to 10min.).
The volatiles will be analyzed on-line by our advanced photoionisation mass spectrometer and off-line by high resolution mass spectrometry and GC/MS. Chars will be characterized by NMR and various imaging techniques.
Other devices (like captive, fixed or micro-fluidized beds) will be also used.
The kinetics of macromolecules pyrolysis will be modeled by lumped models and optimized based on our experiments. Mass and heat transfers in biomass cell walls and particles will be modeled by advanced approaches developed in USA.

Novelty

This project presents important novelties on:

- the laser device will enable for the first time simultaneous on-line analysis, temperature and particles imaging;
- the modeling approach will be very complete including advanced kinetics combined to cell wall and particle scale modeling.



Collaborations

In our laboratory, we collaborate with various researchers on kinetics, imaging, in Metz city on high resolution mass spectrometry, in USA on experiments and modeling (M. Garcia-Perez and other partners).
Stay of at least 6 months (could be 12 months) in USA labs.

Possible profile of the candidate

We look for an engineer or master with skills in chemical engineering, chemistry and/or energy, with a strong wish to work on an interdisciplinary topic linking biology (cell walls of biomasses), heat transfers, optic (laser), analytical chemistry and chemical kinetics.

How to apply

Submit before 10th July 2022, on the website:
https://www.adum.fr/as/ed/voirproposition.pl?site=lorraine&matricule_prop=40565&langue=en

Transcript of records of master or engineering degree, for the last 2 years, with ranking
Detailed topic of the master research project of the last year
CV and motivation letter
Recommendation letters of master or research project supervisor.

References

[1] Global Bioenergy Supply and Demand Projections: A working paper for REmap 2030. /Publications/2014/Sep/Global-Bioenergy-Supply-and-Demand-Projections-A-Working-Paper-for-REmap-2030 n.d. /publications/2014/Sep/Global-Bioenergy-Supply-and-Demand-Projections-A-working-paper-for-REmap-2030 (accessed February 3, 2020).

[2] Alakangas E, Junginger M, van Dam J, Hinge J, Keränen J, Olsson O, et al. EUBIONET III—Solutions to biomass trade and market barriers. Renewable and Sustainable Energy Reviews 2012;16:4277–90. https://doi.org/10.1016/j.rser.2012.03.051.

[3] Access to clean cooking – SDG7: Data and Projections – Analysis. IEA n.d. https://www.iea.org/reports/sdg7-data-and-projections/access-to-clean-cooking (accessed February 3, 2020).

[4] Li C, He Q, Schade J, Passig J, Zimmermann R, Meidan D, et al. Dynamic changes in optical and chemical properties of tar ball aerosols by atmospheric photochemical aging. Atmos Chem Phys 2019;19:139–63. https://doi.org/10.5194/acp-19-139-2019.

[5] van Vuuren DP, Deetman S, van Vliet J, van den Berg M, van Ruijven BJ, Koelbl B. The role of negative CO2 emissions for reaching 2 °C—insights from integrated assessment modelling. Climatic Change 2013;118:15–27. https://doi.org/10.1007/s10584-012-0680-5.

[6] Dufour A. Geological Sequestration of Biomass Char to Mitigate Climate Change. Environ Sci Technol 2013;47:10106–7. https://doi.org/10.1021/es4036418.

[7] Anca-Couce A. Reaction mechanisms and multi-scale modelling of lignocellulosic biomass pyrolysis. Progress in Energy and Combustion Science 2016;53:41–79. https://doi.org/10.1016/j.pecs.2015.10.002.

[8] Wang S, Dai G, Yang H, Luo Z. Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review. Progress in Energy and Combustion Science 2017;62:33–86. https://doi.org/10.1016/j.pecs.2017.05.004.

[9] Pecha MB, Arbelaez JIM, Garcia-Perez M, Chejne F, Ciesielski PN. Progress in understanding the four dominant intra-particle phenomena of lignocellulose pyrolysis: chemical reactions, heat transfer, mass transfer, and phase change. Green Chem 2019;21:2868–98. https://doi.org/10.1039/C9GC00585D.

[10] Mettler MS, Vlachos DG, Dauenhauer PJ. Top ten fundamental challenges of biomass pyrolysis for biofuels. Energy Environ Sci 2012;5:7797–809. https://doi.org/10.1039/C2EE21679E.

[11] Thunman H, Leckner B. Thermal conductivity of wood—models for different stages of combustion. Biomass and Bioenergy 2002;23:47–54. https://doi.org/10.1016/S0961-9534(02)00031-4.

[12] Lédé J, Authier O. Characterization of biomass fast pyrolysis. Biomass Conv Bioref 2011;1:133–47. https://doi.org/10.1007/s13399-011-0014-2.

[13] Dufour A, Castro-Díaz M, Marchal P, Brosse N, Olcese R, Bouroukba M, et al. In Situ Analysis of Biomass Pyrolysis by High Temperature Rheology in Relations with 1H NMR. Energy Fuels 2012;26:6432–41. https://doi.org/10.1021/ef301310x.

[14] Yanez AJ, Natarajan P, Li W, Mabon R, Broadbelt LJ. Coupled Structural and Kinetic Model of Lignin Fast Pyrolysis. Energy Fuels 2018;32:1822–30. https://doi.org/10.1021/acs.energyfuels.7b03311.

[15] Ranzi E, Debiagi PEA, Frassoldati A. Mathematical Modeling of Fast Biomass Pyrolysis and Bio-Oil Formation. Note I: Kinetic Mechanism of Biomass Pyrolysis. ACS Sustainable Chem Eng 2017;5:2867–81. https://doi.org/10.1021/acssuschemeng.6b03096.

[16] Anca-Couce A, Scharler R. Modelling heat of reaction in biomass pyrolysis with detailed reaction schemes. Fuel 2017;206:572–9. https://doi.org/10.1016/j.fuel.2017.06.011.

[17] Montoya J, Pecha B, Janna FC, Garcia-Perez M. Single particle model for biomass pyrolysis with bubble formation dynamics inside the liquid intermediate and its contribution to aerosol formation by thermal ejection. Journal of Analytical and Applied Pyrolysis 2017;124:204–18. https://doi.org/10.1016/j.jaap.2017.02.004.

[18] Kersten S, Garcia-Perez M. Recent developments in fast pyrolysis of ligno-cellulosic materials. Current Opinion in Biotechnology 2013;24:414–20. https://doi.org/10.1016/j.copbio.2013.04.003.

[19] Eitelberger J, Hofstetter K. Prediction of transport properties of wood below the fiber saturation point – A multiscale homogenization approach and its experimental validation: Part I: Thermal conductivity. Composites Science and Technology 2011;71:134–44. https://doi.org/10.1016/j.compscitech.2010.11.007.

[20] Pecha MB, Ramirez E, Wiggins GM, Carpenter D, Kappes B, Daw S, et al. Integrated Particle- and Reactor-Scale Simulation of Pine Pyrolysis in a Fluidized Bed. Energy Fuels 2018;32:10683–94. https://doi.org/10.1021/acs.energyfuels.8b02309.

[21] Teixeira AR, Mooney KG, Kruger JS, Williams CL, Suszynski WJ, Schmidt LD, et al. Aerosol generation by reactive boiling ejection of molten cellulose. Energy Environ Sci 2011;4:4306–21. https://doi.org/10.1039/C1EE01876K.

[22] Jia L, Le Brech Y, Mauviel G, Qi F, Bente-von Frowein M, Ehlert S, et al. Online Analysis of Biomass Pyrolysis Tar by Photoionization Mass Spectrometry. Energy Fuels 2016;30:1555–63. https://doi.org/10.1021/acs.energyfuels.5b02274.

[23] Rabus JM, Simmons DR, Maître P, Bythell BJ. Deprotonated carbohydrate anion fragmentation chemistry: structural evidence from tandem mass spectrometry, infra-red spectroscopy, and theory. Phys Chem Chem Phys 2018;20:27897–909. https://doi.org/10.1039/C8CP02620C.

[24] Oliveira LP de, Hudebine D, Guillaume D, Verstraete JJ. A Review of Kinetic Modeling Methodologies for Complex Processes. Oil Gas Sci Technol – Rev IFP Energies Nouvelles 2016;71:45. https://doi.org/10.2516/ogst/2016011.

[25] Muraille L, Aguié-Béghin V, Chabbert B, Molinari M. Bioinspired lignocellulosic films to understand the mechanical properties of lignified plant cell walls at nanoscale. Sci Rep 2017;7:44065. https://doi.org/10.1038/srep44065.

[26] Oh MS, Peters WA, Howard JB. An experimental and modeling study of softening coal pyrolysis. AIChE Journal 1989;35:775–92. https://doi.org/10.1002/aic.690350509.

[27] Ciesielski PN, Crowley MF, Nimlos MR, Sanders AW, Wiggins GM, Robichaud D, et al. Biomass Particle Models with Realistic Morphology and Resolved Microstructure for Simulations of Intraparticle Transport Phenomena. Energy Fuels 2015;29:242–54. https://doi.org/10.1021/ef502204v.