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

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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]
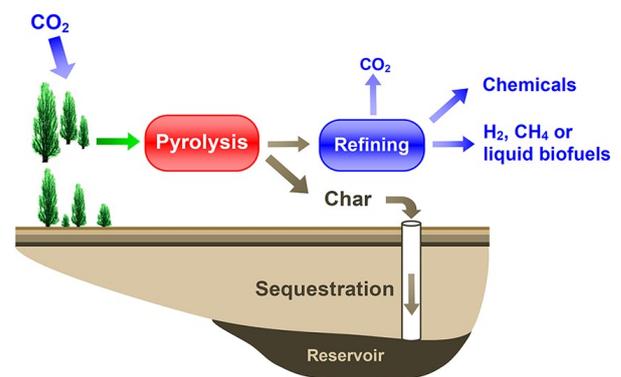
Why it is important to study biomass pyrolysis:

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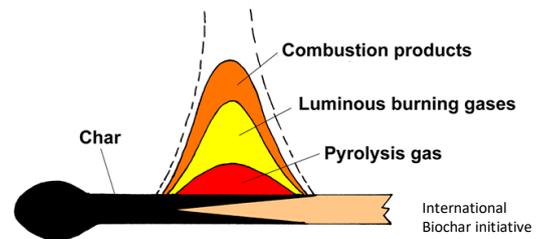
2) Pyrolysis is an important process for carbon sequestration and biofuels production

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]).
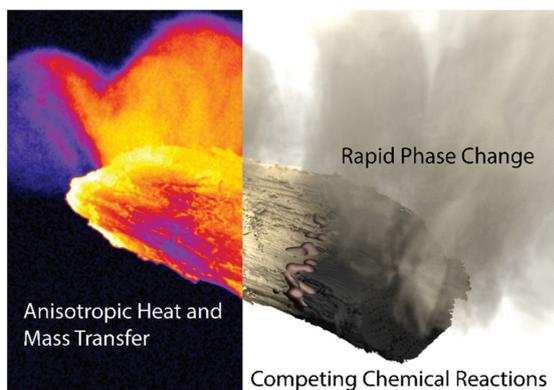
1) Heat transfers

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 developed 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.
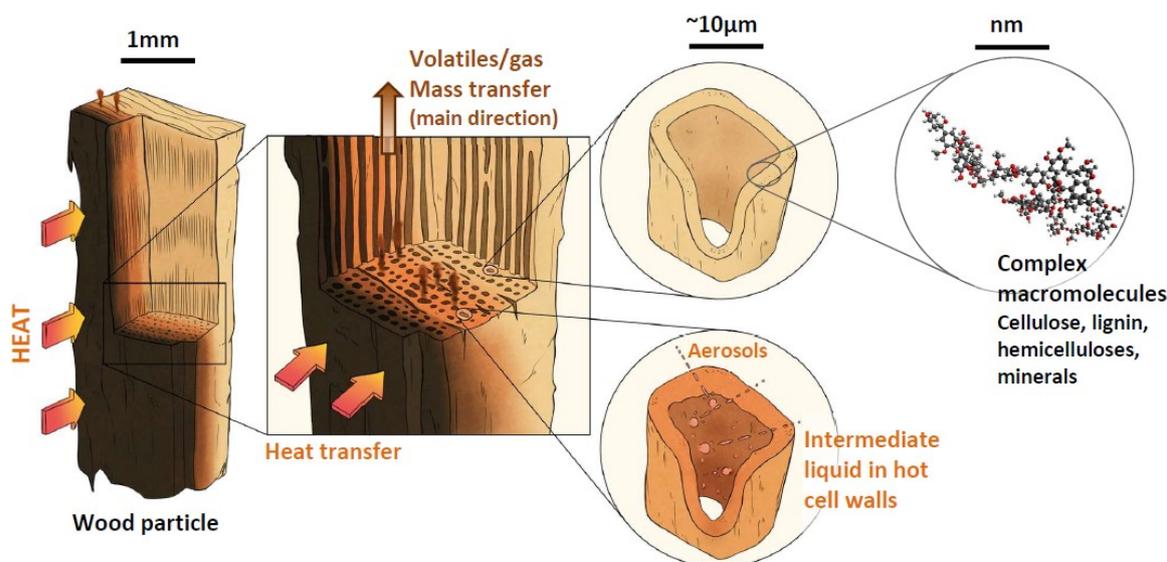
Herein, heat is brought by only one side of the particle in order to highlight the thermal gradient inside the particle and the chemical profile from char to pristine (not converted) wood. In reactor, heat is brought all around the external surface of the particle and is better conducted along the fibers' 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.
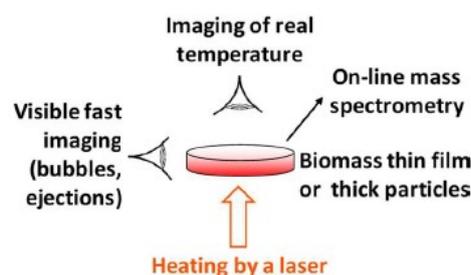
Collaborations
In our laboratory, we collaborate with various researchers on kinetics, imaging, in Metz city on high resolution mass spectrometry, in USA on experiments and modeling (M. Garcia-Perez and other partners).
Stay of at least 6 months (could be 12 months) in USA labs.

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 15th June 2022, on the website:

http://doctorat.univ-lorraine.fr/fr/les-ecoles-doctorales/simppe/offres-de-these/pyrolysis-biomass-advanced-experiments-and-modeling

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.

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