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THE DIFFERENT SCALES OF THE THERMOCHEMICAL PROCESSING OF LIGNO-CELLULOSIC BIOMASS: CASE STUDIES

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Abstract. A general overview of the different routes for a thermochemical valorisation of lignocellulosic biomass is presented. The different scales involved range from the molecular level to the particle level, then to the reactor level, to the plant level and to the forest management. The work done at these levels will be illustrated by examples from two routes: the production of electrical energy and heat by gasification, and the production of BTX by pyrolysis of lignin from biorefinery followed by Hydrodeoxygenation.

Key-words. green process, ligno-cellulosic biomass, gasification, pyrolysis, HDO.

Even if the prices of fossil fuels are currently on the decrease, it is highly probable that the oil peak is behind us. The coal and shale oil and gas reserves are still huge, but all these energy and base chemical sources produce large amounts of CO₂ and the global warming will have dramatic consequences for the future generations. Replacing fossil fuels as far as possible by renewable ones is a duty for our generation. A part of the mix that should ensure a sustainable development is the use of biomass, either to produce electrical energy, or to produce valuable products.

Fig. 1 presents a global view of the chemical and energetic processes that can be used to upgrade different kinds of biomass, as seen by Gillenwater (Lanza Tech)¹. Among the routes presented, only the upgrading of ligno-cellulosic biomass will be considered here, the ligno-cellulosic biomass being either wood residues or “energy” plants like miscanthus.

CASES CONSIDERED

Two cases will be discussed here:

- The use of wood residues to produce syngas, that will be used to produce power and heat.
- The production of valuable chemicals by hydrotreatment of lignin obtained from wood.

Biomass gasification CHP process

Fig. 2 presents a schematic description of the whole route of such as it is investigated in our team. Evaluating such route and designing the different parts of equipment requires a interdisciplinary approach combining investigations at a number of scales:

- Production of the biomass: biomass that is in competition with food uses has to be avoided (the first generation biofuels are deadend), which leaves either plants dedicated to energy uses (trilicate, miscanthus, etc.) or wood, that of course has also other uses (furniture, construction, chemicals). The management of forests has been the subject of a considerable amount of research, also interdisciplinary (climate, sun irradiation, plant biology, etc.), that would be a subject by itself. This has been treated by our colleagues from forest science²⁻⁴: a Java-programme platform called CAPSIS hosts a number of forest

growth models. It also includes a number of diagnostic tools (among which a Carbon Assessment tool) allowing to evaluate forest management strategies.

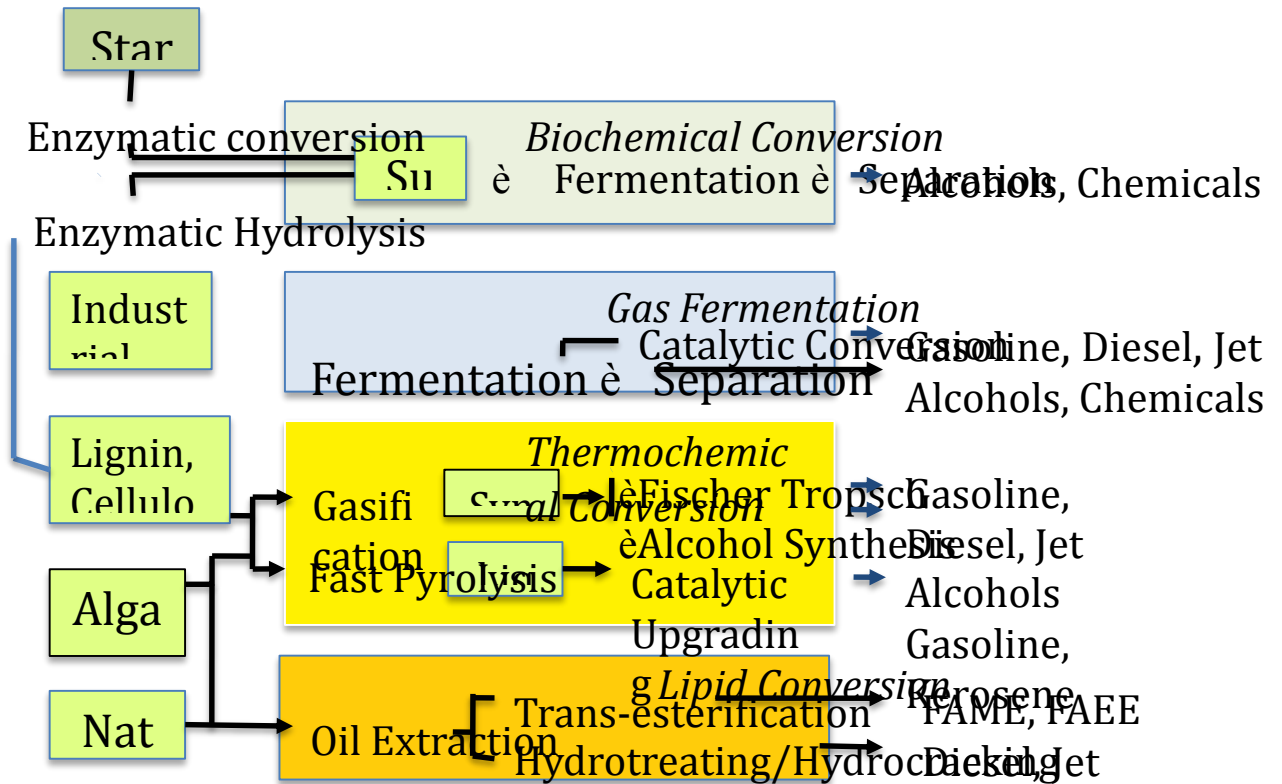


Figure 1: Different routes to upgrade different kinds of biomass (Gillenwater¹)

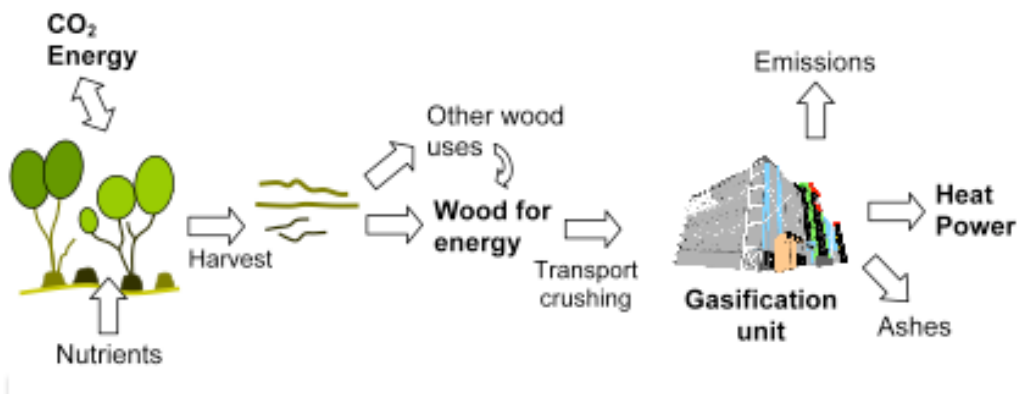


Fig. 2: Schematic description of the route from the production of wood to its use to produce power and heat.

The wood produced is divided according to its quality into different parts, among which the residue is used for energy. The dried wood chips are then gasified in a dual fluidized bed. The latter consists in two interconnected fluidized beds: one for gasification, one for char combustion. In the gasification part, sand is fluidized by a part of the produced syngas, in this part, dry wood chips are converted into gas, char and tar, plus some contaminants (NH₃, HCl, ashes). Gas and char undergo some secondary reactions (mainly hydrocarbon cracking and water gas shift reactions). Char and soot undergo gasification reactions⁴. The dual fluidized bed can take different forms as described in Abdelouahed et al.⁴. Furthermore, one has to include the gas scrubbing, filtration, disposal of ashes, efficiency of the engine to produce electric current. All parts of the process have to be modeled, as well as the whole of the route. Different scales have to be considered: the largest concerns the forest, its management and the reactors. This can be included in a global system (e.g. in ASPEN Plus) allowing to develop a life cycle assessment of the route. This global

program requires models for the different subparts: the fluidized beds, the scrubber, the filtration equipments, the engine, etc... We shall consider only the reactor in this work: the modelling of this equipment requires, beside hydrodynamics and heat transfer, the reaction thermodynamics and kinetics: the pyrolysis (this is the first part of each thermal reaction of pyrolysis), the different other reactions involved.

Production of valuable chemicals by hydrotreatment of lignin

Lignin is the second most important polymer in ligno-cellulosic biomass⁵. It is a by-product of the pulp and paper industry and is available at low prices. In this case, the biomass is separated into cellulose, hemicellulose and lignine, the later two being often considered as wastes.

Fig. 3 presents a possibility of a biorefinery

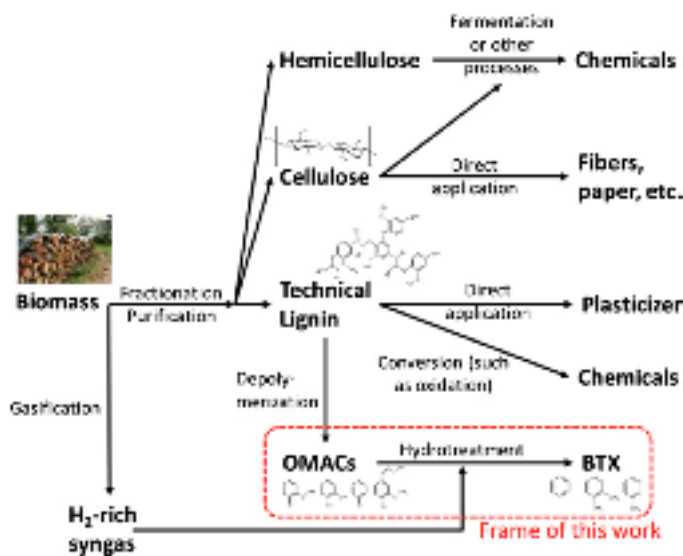


Fig. 3: A possible ligno-cellulosic biorefinery (according Olcese et al.⁶). OMACs: oxygenated mono-aromatic compounds.

Instead of burning the technical lignin produced this way, the possible route investigated in our team by Olcese et al.⁶, consists in depolymerizing the lignin to produce oxygenated mono-aromatic compounds, which then undergo a catalytic hydrogenation (HDO) to produce valuable aromatics (BTX).

SCALES INVOLVED

The simulation of the global route involves a number of scales (from the forest management to the engine via driers, scrubbers etc. Only the reactors will be considered here and even there, the scales involved are manifold.

The reactor scale

A detailed description of a reactor model of a dual fluidized bed gasifier can be found in Abdelouahed et al.⁴. A simplified scheme of the dual fluidized bed gasification reactor investigate by these authors is presented in Fig. 4.

On this figure, a number of reaction steps appear, that have to be considered separately. Part of these can be modeled using a commercial software (in this case Aspen+), part have been modeled separately (indicated as Fortran on Fig. 4). The design rules of the reactor, be it of a hydrogenation fixed bed or a gasification fluidized bed, require “global” kinetics which can be combined with hydrodynamics and transfer phenomena and which can be used for the global modeling of the reactor. These “global” kinetics have to be combined with local hydrodynamics (like it is developed for fluidised beds e.g. by the team of Kuipers⁷).

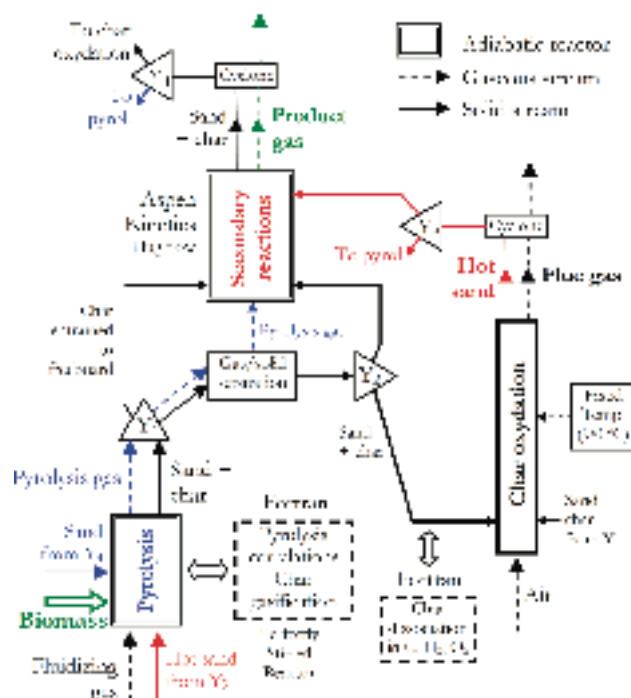


Fig. 4 : Simplified scheme of a dual fluidized bed gasification reactor (Abdelouahed et al.⁴)

In case of HDO reactors, global information on the catalytic reaction kinetics (including the effects of external mass transfer to the particles, diffusion in the particles, poisoning) are required to determine the ideal catalyst particle size, the type of reactor (gas-solid or gas-liquid-solid, slurry, fixed or fluidize bed, cocurrent upflow or downflow) and its size. These global kinetics are often determined in so-called pilot plants and have to be combined with the flow behaviour of the reactor (e.g. in case of high pressure gas-liquid-solid HDO taking into account maldistribution of the liquid as investigated by Llamas et al.⁸).

The particle scale

Models of biomass particles pyrolysis, including heat and mass transfer and chemical kinetics, are developed in our laboratory. Particles are heated by specific devices with a controlled heat flux density (W/m^2) to mimic the thermal conditions of different reactors have been developed. A very efficient tool to this effect is the image furnace described in Christodolou et al.⁹.

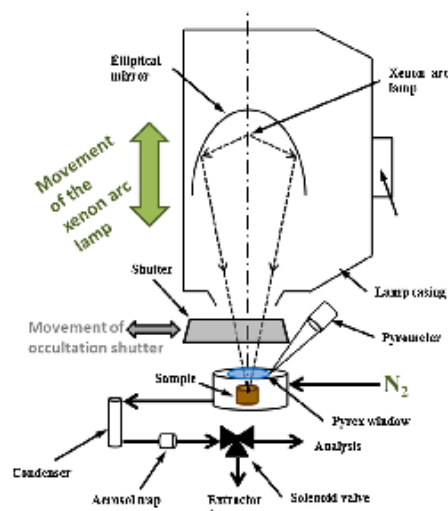


Fig. 5: Pyrolysis in a vertical image furnace (Christodolou et al.⁹)

Global kinetics of catalytic hydrogenation of tar surrogates are made in classical fixed bed reactors (see Olcese et al.¹⁰)

The micrometric scale

At this scale, the mesoscopic behaviour of the wood particles during pyrolysis is observed by a number of techniques: SEM and TEM microscopy (Fig. 6), rheology (Fig. 7), ¹H NMR, Thermogravimetric Analysis (TGA). These investigations prove clearly that during wood pyrolysis, a liquid-like intermediate is formed. These sticky, caramel like intermediates may interfere with fluidization hydrodynamics and a rigorous modeling of this part of the process is not yet possible.

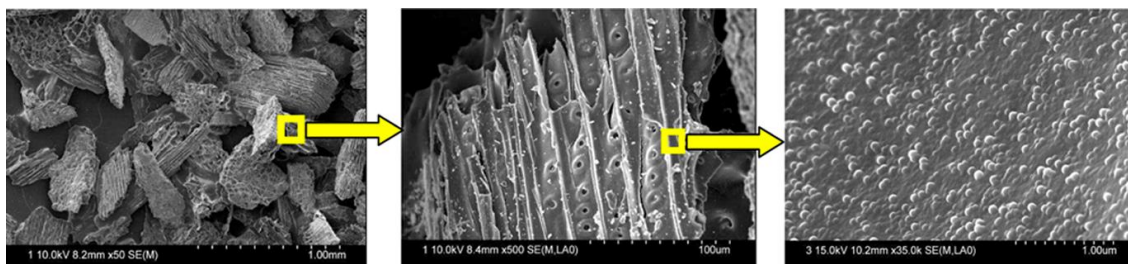


Fig. 6: Wood char particles from mm to μm : bubbles formed at μm scale, even for slow pyrolysis (Dufour et al.,¹¹)

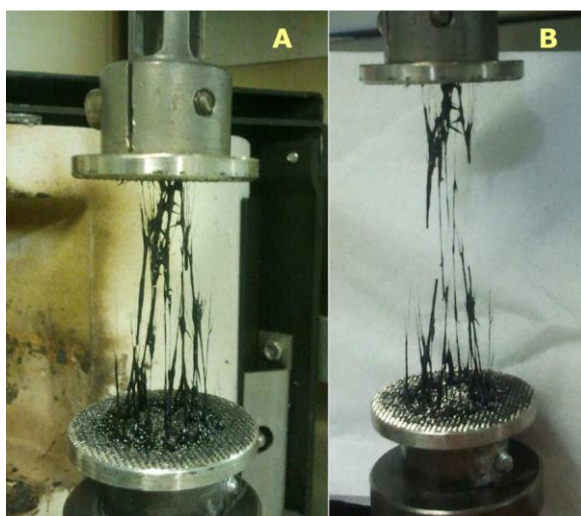


Fig. 7: Photographs of the rheometer plates showing degraded lignin at 200°C: it is a sticky, soft and mainly viscous material like a “hot caramel” (Dufour et al.¹¹).

The microscopic scale

Lignocellulosic biomass as well as its pyrolysis products are complex mixtures, and it is impossible to predict a priori the exact kinetics of the reactions happening, or even the complete mechanisms involved. For this reason, two approaches have been developed:

- implementing advanced in situ measuring techniques to detect not only the pyrolysis products, but also labile intermediates to develop a well funded model. This approach is exemplified by the work of Dufour et al.¹². There a VUV-SPI source (synchrotron radiation) is coupled with a QTOF Mass spectrometer, allowing to detect the fragmentation products of different parts of biomass.

using “surrogates”: the ideal surrogate would be either a pure component or mixture of a limited number of components presenting proprieties similar to that of the pyrolysis product considered. This “surrogate” technique has been applied successfully to the combustion of gasoline¹³ and diesel oil¹⁴. In our group, guaiacol (1-methoxy-phenol) is used as a surrogate for lignin pyrolysis primary tars¹⁵. The kinetics

of catalytic hydrogenation of guaiacol has been extensively studied and an original catalyst has been developed and the catalytic mechanism elucidated by Olcese et al.¹⁵.

CONCLUSION

Figure 8 summarized the different scales at which thermal conversion of lignocellulosic biomass is investigated in our group.

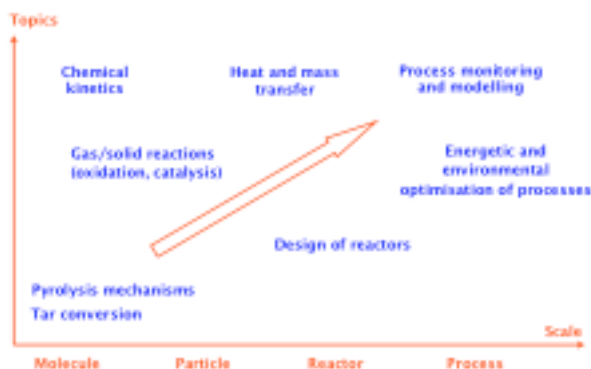


Fig. 8: work done in Nancy in the thermal conversion of lignocellulosic biomass

One point should however not be forgotten: even if all the relevant scales are investigated, the link between the different scales is not always possible. There is still a lot of work to do before being able to predict e.g. the effect of the change of one biomass to another on the performance of a biorefinery or of a gasification system to produce heat and power.

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