Biomass Fast Pyrolysis Reactors: a Review of a few Scientific Challenges and of Related Recommended Research Topics

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Dossier

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Dossier

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Biomass Fast Pyrolysis Reactors: A Review of a Few Scientific Challenges and of Related Recommended Research Topics

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Résumé — **Réacteur de pyrolyse rapide de la biomasse : une revue de quelques verrous scientifiques et d'actions de recherches recommandées** — L'utilisation de la biomasse en tant que ressource énergétique de substitution nécessite sa transformation préalable. De nombreuses options sont possibles. Cet article s'intéresse aux voies thermochimiques et plus spécifiquement à la pyrolyse rapide mise en œuvre pour la préparation d'huiles de pyrolyse. L'optimisation et l'extrapolation des procédés de pyrolyse rapide pour améliorer les rendements et propriétés des huiles de pyrolyse se heurtent à plusieurs difficultés. Le but de cet article est de montrer que certaines sont liées au manque de certaines connaissances scientifiques de base, plus précisément au niveau du réacteur haute température. L'analyse de ces verrous (décomposition thermique d'un grain de biomasse, interactions biomasse-réacteur, réactions secondaires) suggère le développement de plusieurs axes de recherche.

Abstract — ***Biomass Fast Pyrolysis Reactors: A Review of a Few Scientific Challenges and of Related Recommended Research Topics*** — *The use of biomass as an alternative energy resource requires its prior processing. Many options are possible. The present paper focuses on thermochemical routes and more specifically on fast pyrolysis carried out for the preparation of so called bio-oils. The optimization and scaling up of fast pyrolysis processes for improving bio oils yields and properties come up against several difficulties. The aim of the paper is to show that some of them are related to the lack of several basic scientific knowledges, more specifically at the level of the high temperature fast pyrolysis reactor. The analysis of these challenges (biomass sample thermal decomposition, biomass-reactor interactions, secondary reactions) suggests the development of several research topics.*

NOMENCLATURE

AP	Ablative Pyrolysis
BFB	Bubbling Fluid Bed
BO	Bio-Oils
CFB	Circulating Fluid Bed
FP	Fast Pyrolysis
h	External heat transfer coefficient
HHV	Higher Heating Value
IAC	Intermediate Active Cellulose
RTD	Residence Time Distribution
TGA	ThermoGravimetric Analysis
T_S	Temperature of biomass sample surface
T_W	Heat source temperature
φ	Available heat flux density

INTRODUCTION
THE DIFFERENT ROUTES OF BIOMASS THERMAL UPGRADING

Biomass is one of the most important source of renewable energy. Its thermal decomposition has several advantages including the possibility of upgrading all the major components (cellulose, lignin, hemicellulose) of any type of biomass. Thermochemical processes are usually classified as combustion, gasification and pyrolysis [1, 2]. In combustion, biomass is burned under an excess of O_2 for heat and electricity generations. In gasification, biomass is transformed under lower fractions of O_2 (or of steam) into a syngas (containing a majority of H_2 and CO) that can be further used for several possible applications such as heat generation, H_2 or CH_4 preparations and production of biofuels through Fisher Tropsch synthesis. Pyrolysis processes are usually carried out under inert atmosphere for the production of solids (char), condensable vapours and gases (H_2, CO, CO_2, CH_4, light hydrocarbons) whose fractions and natures strongly depend on operating conditions (types of reactor and of biomass, heating conditions, pre and post-treatments, etc.). In all these thermal processes, the chemical phenomena begin with primary steps of biomass thermal decomposition followed by more or less extended secondary reactions (crackings, repolymerizations, gas phase and gas-solid interactions). The present paper deals with the specific case of Fast Pyrolysis (FP) processes, carried out with the aim to prepare Bio-Oils (BO) after vapours condensation.

1 PROCESSES OF BIOMASS FP GENERAL CONSIDERATIONS

To be noticed that the same word "pyrolysis" is unfortunately used in the literature for designing both the basic phenomena of biomass primary thermal decomposition and also the whole process.

1.1 General Description of FP Processes and Aims of the Paper

A FP process usually comprises the different following steps designed in order to enhance BO production [1, 2]:
- biomass harvesting, handling, storage, pretreatment (drying, grinding, etc.) and any other operations imposed by the type of FP reactor;
- feeding of the reactor;
- high temperature FP reactor which is the heart of the process and where pyrolysis is carried out;
- several steps of products processings including more or less fast coolings, separations, cleanings and also partial recycling of by products in order, for example, to provide process heat;
- BO storage and further post treatments.

Reliable optimization and scaling up of these FP processes, for BO yields and qualities improvements, comes up against a great number of difficulties. The purpose of the paper is to show that some of them are related to the lack of several basic scientific knowledges. We shall mainly examine the case of FP reactors. The most important involved phenomena will be described and studied according to a decoupled approach. They include those occurring at the biomass particle level and with the surrounding, and those connected to the own nature of the reactor. Their couplings will be underlined. We shall see that many of them are still not fully understood. Related recommended research topics will be suggested in each case. A description of most usual FP reactors, as well as their related advantages and drawbacks, will be then reported. The reader will easily find additional details in other more specific papers or reviews which will be cited. The paper ends with a very brief description of other needed research actions related to other steps of whole FP processes (*i.e.* upstream and downstream of the reactor, such as biomass pretreatment and products post treatments).

1.2 Conditions Required for FP

Pyrolysis is often classified into slow, intermediate and FP [1, 2]. In the first case, the production of a solid phase (char) is enhanced. Gases and condensible vapours are a majority in FP. Slow pyrolysis is known since several millennia while FP is mainly considered since the 1975-1980's [3], even if the differences between these two types of pyrolysis have been already noticed as soon as the end of the 1870's [4]. The conditions required for intermediate pyrolysis are more obscure. No quantitative frontier

exists and there is probably a continuum between all these types of pyrolysis. The notion of flash pyrolysis is sometimes used in the literature [5]. However the differences between fast and flash pyrolysis are not clear and we shall not make any distinction between them.

The literature reveals the existence of several possible requirements to be fullfiled for FP [2, 6, 7]. Unfortunately, the usual criteria depend on the authors, making difficult the comparison of different experimental systems on a same basis. In addition, these criteria, such as heating rate and temperature are rarely quantitatively defined and moreover may be at the origin of important mistakes. Also, the sometimes recommended condition to work with small biomass particles is not valid in any type of FP process. In a recent paper, Lédé and Authier [8] have shown that, in order to be able to compare different experimental conditions on a same basis, the enhancement of BO fractions is favoured if two conditions are fulfilled at the biomass sample level: high external heat transfer coefficient and efficient primary products removal. All these points will be discussed in further sections of the present paper.

2 BASIC PHENOMENA OCCURRING INSIDE FP REACTORS

A great number of basic phenomena occur inside the reactor. Their study is however difficult because of the existence of close couplings between them. We shall successively distinguish the three following main locations:

- reaction of a single biomass sample liberating primary products;
- biomass sample-reactor interactions: external heat and mass transfer efficiencies, as well as reactor hydrodynamics;
- secondary reactions underwent by the primary pyrolysis products inside the reactor.

2.1 Thermal Decomposition of a Biomass Sample

2.1.1 General Considerations

A best understanding of the primary phenomena occurring at the level of each single biomass particle is required because they can control several subsequent reactions. These data are essential for further scaling up and for calculating the decomposition rate and hence the time of complete particle (of a given size) reaction (for example, this time should be compatible with particle residence time in the reactor).

Schematically, a biomass sample submitted to a given external heat flux density undergoes several physicochemical transformations. It is firstly heated from inlet (room) temperature until the temperature (or narrow domain of temperatures) at which chemical reactions (pyrolysis) occur according to complex kinetics pathways. According to the size of the sample, internal heat transfer resistances may control or not the apparent rate of reaction because of the low biomass thermal conductivity and the rapidity of basic chemical reactions. These aspects will be described in a following section.

2.1.2 Biomass Pyrolysis Kinetics

An extensive number of works have been published since the mid of the 19th century in the field of biomass (and mainly cellulose) thermal decomposition [3]. The first kinetics results appeared much later (around 1950). In spite of a considerable amount of published results, there is no clear consensus in the literature for describing kinetics pathways and constants that could be valid in any situation. The main reasons are:

- each biomass type has its own composition and hence specific different physicochemical properties. For example, the fractions of the main basic components (cellulose, lignin, hemicellulose), as well as inorganic contents (that may play significant catalytic roles) may greatly differ according to the origin of biomass;
- basic kinetic behaviours are, most of times, determined at the laboratory scale. The experimental conditions under which the measurements are made may differ from an author to another, for example: from fixed to entrained beds; from a fixed (and more or less high) heat source temperature to conditions of increasing outside temperature (as for example in ThermoGravimetric Analysis (TGA)); from small to large biomass samples; more or less efficient thermal quenching of the primary products. In addition, the measured parameters and hence, types of interpretations, may also differ according to the authors, facilities and objectives: sample mass loss; complete or partial determination of the three phases fractions (problem of reliable estimation of mass balances); analysis of products compositions; different types of temperatures measurements or estimations. A consequence is the difficulty to compare results obtained by different laboratories;
- the models expected to represent the experiments may be more or less sophisticated according to the simplificated assumptions and uncertainties made on the values of several physical constants;
- Arrhenius kinetic constants are derived from so called reaction temperature which is often very badly known (see below).

Model Compounds

Because of the complexities and varieties of biomasses, a majority of works has been performed with cellulose, often considered as a model compound. Its mass fraction in biomass roughly ranges between 40 and 50% (on dry basis). It is a well known high molecular weight linear polymer of β-(1-4)-D-glucopyranose units linked by (1-4)glycosidic bounds [6]. Several hundred papers have been published on its thermal decomposition and even in this simple case no actual consensus is reached in the literature. In a recent historical review, the great number of main published kinetic schemes is described [3]. They include simple lumped models (relying on the only basis of the different fractions involved: permanent gases, condensable vapours, solids) until detailed mechanistic models (including radical and ionic reactions). A very large range of complexities are considered: from very simple schemes (for example one single step process) until models including a network of several subsequent reactions (occurring in the gas and/or liquid phases, fluid-solid interactions). Most of the elementary processes include dehydrations, fragmentations and repolymerizations. As soon as the 19th century, levoglucosan has been shown to be one of the main final product (its formation is in competition with that of hydroxyacetaldehyde). However it is now accepted that it is not a primary species. Since several decades the literature reveals controversies as for the existence of primary intermediate short life time species (Intermediate Active Cellulose, IAC). IAC formation is accompanied with phase change phenomena in FP conditions. IAC gives subsequently rise to more stable products such as gases, vapours and char. The existence of IAC is now well established. However, because of its short life time (a few tens of ms in FP conditions), its properties are still badly known (is it partially decomposed cellulose or simple melted cellulose; which degree of polymerization; which chemical composition; which kinetics of formation and decomposition). These properties also vary according to the operating conditions. Many research efforts are needed. The problem of IAC is not a simple academic concern as the existence of an intermediate liquid phase (also evidenced for biomass itself) may have important effects in the behaviour of FP reactors because of stickings and plugging phenomena. Also, its vapourization process influences vapours (and hence BO) yields. IAC is also at the basis of the so called Ablative Pyrolysis (AP) (see below for biomass). The Broido Shafizadeh model [9] (established for cellulose at the end of the 1970's from TGA measurements) has been and continues to be one of the most often used kinetic model. It relies on the primary existence of IAC that subsequently gives rise to two competitive reactions (formation of vapours and char + gases). All these problems are discussed in a recent review [3].

It is well established since a long time that the concentrations and natures of inorganic species have strong impacts on the cellulose pyrolysis reactions. Many works have been made in TGA (slow pyrolysis) and less in FP conditions [10]. They all agree to show that the presence of inorganics usually increases char and decreases vapours (and hence BO) yields and also rates of mass loss. The gases composition is also changed (for example increase of H_2 fractions and decrease of CO fractions in the cases of K, Zn, Ni and Mg). The natures and structures of char are also modified. The presence of inorganics induces also an increase of IAC production. The mechanisms of inorganics reactions continue to give rise to research actions.

To be noticed that in severe FP conditions, pure cellulose gives rise to negligeable fractions of char, with formation of very high fluid products yields [11, 12].

Much less works have been published with other biomass major components (hemicellulose, lignins). Here also, they have been mainly performed in slow pyrolysis conditions. Xylan (poly β-D-xylopyranose) is often used for simulating hemicellulose behaviour. For lignins (a polymer of methoxylated phenylpropane units) important problems result from the difficulties to extract lignins in their native form and to prevent related deep modifications of lignins structures. A consequence is that lignins properties strongly depend on the various types of extraction processes (for example: Borregaard, Kraft, Lignotec, OCL, Avidel). The yields of gases, vapours and char may vary with a factor of up to 4 according to the type of lignin [13]. The fractions of H_2 and CO may also be very different. Guaiacol is often used as a model compound of lignin pyrolysis vapours [14]. Lignins pyrolytic behaviours depend also on their inorganics contents (connected to inorganics contents of biomass from which they have been extracted and to inorganics involved during the extraction processes). It is hence difficult to study their influences (usually less important than in the case of cellulose). Impregnated lignins produce less vapours and gases but produce gases with higher H_2 fractions [10]. As in the case of cellulose, xylane and lignins also primarily pass through the formation of intermediate liquid species.

The experimental comparison of cellulose, xylane and lignins pyrolytic behaviours shows that cellulose produces the highest fractions of vapours and only few char. Lignin produces the highest yields of char and gases with highest H_2/CO ratios. The most marked inorganics influence is observed for cellulose. The literature often reports the different temperature domains under which

these three components react. However these results are most of times obtained in slow pyrolysis conditions and cannot be extended to FP (higher reaction temperatures domains) where the studies are much more difficult because of the rapidity of the phenomena.

Biomass

Numerous results are also available in the literature. However each ones are related to given types of biomasses and experimental conditions of heating. Thus their validities for other situations can be questioned. Sometimes the results obtained with cellulose are used for representing biomass itself [15]. It is for example the case of the Broido Shafizadeh model. However, in order to take into account the variations of char, vapours and gas fractions, global kinetic models including three parallel reactions (giving respectively rise to char, vapours and gases) directly formed from biomass can be used [16, 17]. The three corresponding kinetic constants may be obtained through optimization procedures [18]. These simple models usually do not include the intermediate passage of biomass through a fluid phase which, however, has been evidenced since a long time [19]. These results which are only valid inside given conditions, can be useful for reactor upscaling.

The primary reaction giving rise to a fluid phase (and at the basis of AP) has been shown to occur at a relative constant temperature of around 773 K. This phenomenon has been referred to fusion like behaviour of biomass [20].

Several authors have tried to represent the pyrolytic behaviour of a given (natural) biomass on the basis of those of its main components (cellulose, lignin, hemicellulose) and of their fractions. Here also much more results have been obtained in TGA than in FP conditions [13]. One of the difficulties is to define the basis on which these (linear) combination rules should be established: mass loss; char/vapours/gases fractions; kinetic constants; physical properties or gas composition. The results of such theoretical combinations can be compared to those experimentally obtained with simple mixtures of model components and also with actual biomass behaviour. The agreements are better if the comparisons do not rely on simple experimental results but on the basis of mathematical models where combination rules are, in addition, written also for the different physical constants of all involved components. In any case, these combination rules should be tested in conditions minimizing the secondary reactions (such as gas phase crackings). Consequently, combination rules written on the simple basis of gas composition should be cautiously considered. In any case, the discrepancies observed between theoretical previsions and actual experimental observations result from the existence of interactions (catalytic or not) between the main components inside the natural biomass structure. These phenomena are still badly understood.

The presence of inorganics in biomass (such as K, Ca, Na, Mg) also considerably modifies the kinetics of biomass FP, reaction selectivities and BO chemical composition [10]. As in the case of cellulose (see above), they induce an increase of char fraction (and modification of its structure), a simultaneous decrease of vapours yields (and hence of BO) and rate of sample mass loss. The nature of intermediate fluid compound is also modified. These phenomena can be clearly evidenced from experiments made with a given type of biomass which has been previously impregnated with inorganic salts, or whashed for eliminating its inorganic content [10]. A result is that biomasses with high natural ash contents (straw for example) produce less vapours (and hence BO) than wood.

To be noticed that the inorganics which are present in biomass may be transported out of the FP reactor inside fine char particles and/or aerosols droplets (directly issued from the reacting biomass sample or through subsequent vapours condensations). Parts of these released inorganics can be recovered in BO, with resulting modifications of their properties (stability for example) [21].

Remarks

From the above known results it appears that a great number of BO compositions may exist according to the reactor, the operating conditions and mainly the type of biomass (wood, bark, agricultural residues, algae, forest residues, lignins, cellulose). These observations, that should be more accurately taken into account, imply high flexibilities for reactor operation, post treatments steps, and BO uses.

The kinetics of elementary processes are often supposed to be of first order and to obey simple Arrhenius types laws.

The enthalpies are known with poor accuracies. The available values are often valid for the global FP reaction (endothermal). Those related to elementary chemical processes are more scarce. For a given kinetic scheme, some ones are endothermal and others exothermal (for example char formation). Here also, direct (difficult) measurements in FP conditions are recommended.

2.1.3 Transfer Processes Occurring near the Outside Surface of a Reacting Biomass Sample [8, 22]

The heat flux densities required for biomass FP can be of different natures. According to the type of reactor, the

heat exchanges may occur through convective (hot gas/sample), radiant (hot neutral or catalytic particles, walls) and/or conductive (more or less direct contact with a hot surface) processes. The heat source can be at a fixed temperature (T_W) as in the case of most continuous reactors or at a temperature increasing with time (imposed outside heating rate as in TGA for example). In the first case and in the assumption of a given heat transfer coefficient h, the available heat flux density φ at the particle surface (temperature T_S) is equal to $h\ (T_W - T_S)$. This expression shows that φ is not a constant criterium because of the time evolution of T_S which increases from inlet biomass temperature (often ambient) until reaction temperature. The result is that, mainly for moderately high values of T_W, φ can strongly decrease as the sample is heated and reacts. Hence, the FP severity decreases with time. For example, for a value of T_W around 873 K and having in mind that FP occurs around 773 K, the value of φ diminishes with a factor higher than 5. When approaching the end of the process φ even tends to 0 when the char layer reaches external temperature T_W. The phenomena are still more complex in the case of radiant exchanges: the value of φ depends on changing surface emissivity (biomass to char) and h depends also on T_S. In addition the external heat flux transferred by conduction inside large biomass samples decreases also (mainly because of formation of char having a lower thermal conductivity than biomass). So, for large biomass samples, the beginning of reaction (peripheral sample layers) may occur in FP conditions while, after a certain time, the central parts may react in conditions of slower pyrolysis (hence producing more char, less vapours and hence less BO).

Consequently, because of its variability, the heat flux density does not seem to be a satisfying criterium for defining FP. Conversely, the outside heat transfer coefficient which is a characteristics of the reactor (in the cases of convective and conductive exchanges) appears to be more pertinent. FP severity increases with h [8].

In these previous cases, the pyrolysis primary products escape out of the sample through different possible elementary processes. They mainly include: vaporization of fluid intermediate species formed in the first stages of pyrolysis; high speed ejection of small droplets (aerosols); convective transfers. Secondary reactions which are still badly understood can occur during these processes. Similarly, primary vapours can also undergo secondary reactions during their transfer through hot char layer whose thickness increases with time (in the case of large biomass samples). These reactions include for example vapour/char heterogeneous reactions that can give rise to additional char. All these secondary reactions can modify BO properties and yields. Finally, it could be theoretically expected that attrition phenomena would be advantageous. Accordingly, continuous char layer elimination would theoretically prevent the extent of these heterogeneous processes and also allow more constant conditions of high heat transfers efficiencies. Hence vapours fractions could be theoretically enhanced. Conversely, the simultaneous formation of fine char particles may induce vapours-char interactions in the gas phase and their presence in the condensed fractions may also reduce BO qualities. It is hence clear that all these basic phenomena that induce BO modifications need to be better understood.

A specific case of FP is the so called Ablative Pyrolysis (AP) where biomass is pressed against a hot (metallic or catalytic) surface [19]. The heat transfer mainly occurs through conductive processes. The very high heat transfer coefficients (much higher than 10^3 $W{\cdot}m^{-2}{\cdot}K^{-1}$) are proportional to the contact pressure. In addition, the apparent reaction rate increases with increasing relative velocity between biomass and hot surface. The biomass consumption rate may reach a few 10^{-2} $m{\cdot}s^{-1}$ while the reactional thickness zone is of a few tens of μm. The heat transfer occurs through a very thin liquid layer (primary products of biomass FP reaction). Because of the relative velocity between biomass and surface, these liquids are efficiently eliminated and the reaction rapidly occurs in steady state regime. The thin fluid film acts also as a lubricant. In optimal conditions, AP produces very low char fractions and mainly vapours (maximum BO production) providing that vapours secondary crackings are avoided. Practically, contact AP is mainly destined to large biomass samples (hence preventing costly grindings operations). Clearly, the required condition of fine particles, often recommended for FP, is not valid in the case of AP.

Finally, it is possible to operate under conditions of imposed heat flux densities. These devices rely on the use of a concentrated radiation provided by a high intensity arc image (or sun) associated to one or several concentrating mirrors [11, 12, 23]. One of the advantages is that secondary reactions in the cold gas phase are avoided because the carrier gas does not significantly absorb radiation.

It appears that, in all the above situations of various heat transfer types, the maximization of vapours fractions needs efficient elimination of primary products of reaction which are mainly liquids in FP. A conclusion is that FP is favoured (enhancement of BO fractions) if two necessary conditions are simultaneously fulfilled: high external heat transfer coefficient and efficient primary products removal. These two parameters can be recommended as being reliable criteria for comparing,

on the same basis, the behaviours of biomass samples undergoing FP in various heating conditions [8].

2.1.4 Actual Biomass Pyrolysis Temperature and Heating Rate [8, 24]

The knowledge of the reaction temperature is essential for the determination of kinetic laws (for example: Arrhenius constants). Moderately high temperatures and high values of heating rates are usually recommended for the characterization of FP. However, the authors rarely specify at which level, these two parameters are defined: pyrolysing biomass sample or heat source (gas medium, hot surface or reactor walls)? Reaction temperature is often expected to be close to that of the heat source, leading to important mistakes (see below). Also, important temperature gradients may exist inside the reactor. Schematically, the biomass reaction temperature results from an equilibrium between heat demand (heat required by biomass according to given kinetic laws for a globally endothermal reaction) and the external available heat flux provided by the heat source. Consequently the actual reaction temperature has few chances to be similar to that of the external heat source (even for very small sizes particles). If the notion of heating rate is well known in TGA it is, on the other hand, very difficult to define in other cases of FP continuous reactors operating with a fixed heat source temperature and whatever biomass particles sample (see below). In addition, temperature and heating rate are usually very difficult to experimentally measure at the biomass sample level for the main following reasons:

- FP reactions are very fast (sometimes lower than 1 s). Very small response times measuring instruments are required;
- on line temperature measurement of fine and rapidly moving particles is also almost impossible;
- high temperature of the heat source may influence the measurements;
- it is not always easy to ensure a close contact between the sample and a thermocouple.

The determination of temperature and heating rate needs the solving of mathematical models [22] relying on heat and mass balances at the biomass level. The complexities of the models depend on the level of simplifications in the choice of assumptions (type of kinetic scheme, taking or not into account internal mass transfer resistances, etc.). Another difficulty concerns the choice of physical constants. Actually, the reactions involve three phases: solids (biomass and char), liquids (short life time intermediate species) and gases. The compositions, properties and fractions of these phases vary during the progress of reaction. The implied physical constants include: heat capacity, thermal conductivity, mass density, diffusivity, radiant properties (emissivity, reflectivity), etc. All the corresponding quantitative values are still very badly known, as well as their evolutions with temperature. Their knowledge needs to be improved.

Two extreme cases are usually considered in the models according to the size of the sample. In the case of a fixed heat source temperature T_W, the results show:

- for particles diameters under approximately a few tens of μm, the Biot number is small and there is no significant internal temperature gradient. Pyrolysis occurs uniformly in the whole particle volume. The pyrolysis rate is hence controlled by chemical processes alone. It is thus relatively easy to derive kinetic data, providing difficult assumptions on the actual particle temperature. The results show that the particle uniform temperature (initially at ambient), increases with time and strongly stabilizes as the reaction begins. This narrow domain of reaction temperature is always lower than T_W (sometimes several 100 K difference). It is hence erroneous to assume that the reaction occurs at T_W even for very fine particles. Consequently, the heating rate is also very difficult to define: it is maximum at the first moments of biomass particle preheating, then it regularly decreases with time, before becoming very low during reaction (stabilization phenomenon) [24];
- for large particles sizes, the temperature varies both with time and location inside the sample. Actually, because of the existence of steep internal temperature gradients, the peripheral sample zones are first heated and hence begin to react while the heart of the sample may be still near room temperature. Then, a reactional front moves from the outside towards the central zones of the sample. The apparent kinetics is now controlled by the poor solid thermal conductivity. It can be also shown that for given outside heat transfer conditions, a small and a large particle do not react at the same temperature making difficult the scaling up of results derived with fine particles. In addition, during the progress of the reaction (moving of the reacting zone) solid products (char) are formed and accumulate, thus progressively reducing the heat flux arriving in the virgin zones of biomass. Then, the central parts react in less and less severe conditions and hence produce less and less vapours. Also, thick char layers may induce vapours-char interactions reducing also vapours yields (possible control by mass transfer resistances). As with small particles, the heating rate cannot be easily defined with, now, the additional difficulty that it varies also with location inside the sample. Finally, it can be shown that heating rate may become very small (similar as in slow

pyrolysis) in the heart of a large sample even in external high heat transfer coefficients conditions [8, 22].

In all the cases, FP reaction occurs inside a stabilized domain of temperatures. Such a behaviour, associated to the passage through an intermediate liquid phase, has led to assimilate FP reaction to a phase change phenomenon [20].

The only cases where sample temperature and heating rate are similar to those of the heat source are encountered in TGA devices operating under imposed temperature and heating rates [25]. Unfortunately, the corresponding conditions (slow pyrolysis) are far from those required for FP.

As a conclusion, the values of biomass pyrolysis temperature and heating rates are very difficult to define and to experimentally measure in FP. They can mainly be obtained from the solving of mathematical models which is also a difficult task because of the high complexity of involved phenomena and of the uncertainties on a great number of chemical and physical constants.

2.2 Brief Description of Other Phenomena Directly Induced by the FP Reactor Itself

The values of heat and mass transfer coefficients as well as T_W are imposed by the reactor (see above). In addition, once liberated by the biomass sample the vapours can undergo more or less extensive secondary reactions inside the gas phase.

2.2.1 Pressure and Dilution Effects

It is well known that the vapours yields increase as the pressure inside the reactor decreases, and also in conditions of high carrier gas flowrates. These observations are explained by dilution effects of primary species and modifications of secondary reactions extents. In addition, primary vapours escape more rapidly from the hot zones of the vessel. The char fractions resulting from secondary vapours – solid reactions are also minimized [26, 27].

2.2.2 Secondary Phenomena

Except in the cases of AP types reactors, the gas phase temperature is usually close or higher than that at which primary biomass pyrolysis occurs. The primary vapours may hence undergo subsequent homogeneous (gas phase) and/or heterogeneous (vapours-solid) reactions. They include crackings (leading to H_2, CO, etc. formation) and also partial repolymerizations and charring reactions. Formation of secondary and tertiary vapours having higher molar masses, lead to lesser BO qualities. However, conversely to these drawbacks, the matured vapours have less oxygen content and hence BO have better Higher Heating Value (HHV). The solids involved in vapours-solid interactions may be biomass ashes, catalysts and/or char particles issued from pyrolysis with more or less inorganics contents. In a recent paper relying on experiments performed in a fluidized bed, Hoekstra *et al.* [28] show that between 673 and 773 K, and for residence times from 1-15 s, the charring repolymerizations reactions are more important with particles of high inorganics contents. It is hence recommended to decrease the contact times between vapours and inorganics for increasing BO qualities. In the case of low ash content chars, homogeneous cracking reactions are more important even if they seem negligeable under 673 K.

These results are in agreement with other papers [2] recommending to operate with vapours residence times lower than 2 s (for temperatures 673-723 K). However, the problem is more complex because the search of optimal conditions preventing secondary reactions needs to optimize both residence times and temperatures values on the basis of reliable cracking kinetic schemes and of pertinent hydrodynamic models. Here also these problems need further research.

Let suppose the simplified case of homogeneous cracking reactions which have given rise to a great number of papers for biomass and cellulose. In the simplified assumption of a first order reaction, the published kinetics constants vary over 2 orders of magnitudes [29]. Actually, the available values depend on a great number of experimental parameters such as: measurements made inside the pyrolysis reactor or separately, types of biomasses or of pyrolysis, reaction in the presence or not of steam, pressure, dilution.

The relevant definition of residence times and temperatures in the reactor is also another difficulty. Uniform temperature and ideal flows are often assumed. Actually, important temperature and velocity gradients may exist inside the gas phase. Actual Residence Time Distribution (RTD) should be taken into account. For example, a stirred tank like behaviour leads to better uniform temperature than a plug flow. In addition, the solid phase (biomass particles) RTD is often quite different than that of the gas phase.

Efficient scaling up of laboratory data should result from the modeling of all these phenomena (primary and secondary reactions, heat and mass transfer efficiencies, solids and gas phase RTD) and of their close couplings.

We have seen that heat source temperature is rarely the same as that of the reacting biomass sample. It is hence erroneous to assume, as sometimes in the literature, that

secondary gas phase reactions occur at the same temperature as that of primary biomass pyrolysis.

Finally, it is often difficult to extract data related to secondary reactions from those resulting from particle primary pyrolysis, when all these phenomena occur in the same vessel. Decoupled studies are hence recommended.

As a conclusion, these secondary reactions that may highly influence BO yields and qualities should continue to give rise to extensive studies.

3 MAIN TYPES OF FP REACTORS AND CONCEPTS

Many types of reactors can be used for carrying out biomass FP. Several ones rely on the basis of usual gas-solid reactors, even if the FP reaction is of a more specific type where gas-solid secondary interactions should be usually avoided. Only few new reactors concepts have been imagined for the specific case of biomass FP.

Continuous operation can be carried out in small pilots (fractions of kg/h), until large pilot (several hundred kg/h) plants. Some laboratory scale designs operate in non steady state with few mg mass samples. Laboratory reactors may be designed for the only purpose of basic research but with the difficulty to use the results in the modeling of pilot plants operating in different conditions of temperatures and transfers. They may also rely on the same types of facilities as those of larger pilot plants in order to make easier the scaling up. However several difficulties should be overcome. For example, when laboratory results are obtained with particles sizes similar as those used in much larger reactors.

No universal and clear scientific criteria exist for comparing the behaviours of different FP reactors types. We have seen that temperature and heating rate are inappropriate. On a pure fundamental basis, and at the level of biomass sample, high external heat transfer coefficient and efficient primary products removal can be recommended. The global reactor performances too often rely on poorly scientific basis such as maximum biomass throughput.

Followed is a brief description of the main types of FP reactors. More details can be found in several relevant reviews [1, 2, 6].

3.1 Fixed Beds. Devices Operating with a Given Mass of Biomass (Mainly Laboratory Devices)

Fixed beds and related systems usually do not operate in conditions required for FP (low heat transfer coefficients, high vapours residence times) [2]. A great number of kinetic measurements is performed in TGA [25]. However the imposed heating rates are very low (0.1-100 $K \cdot min^{-1}$) and the actual biomass reaction temperatures may be much lower than in usual FP. However the advantages are that because of the very small mass samples used, the reaction occurs in chemical regime and at a well defined temperature. The pyrolysis reaction can be also studied with a few g sample placed inside an horizontal heated tube settled inside a furnace [29]. Biomass is heated by radiative and/or convective transfers with a hot flowing carrier gas. The secondary reactions are minimized thanks to vapours dilution and to their rapid cooling as soon as they leave the tube. The total mass loss of the sample is easily determined while gases and vapours are recovered (allowing the establishment of complete mass balances). The pyrolysis occurs between slow and fast conditions. Finally, very high imposed heating rates (thousand $K \cdot s^{-1}$) can be reached in systems where a very small biomass sample is deposited on a metallic wire which is rapidly heated (electric heating) [30, 31]. Pyrolysis gases and vapours can be analyzed on line. However it has been shown that the actual biomass heating rate is considerably lower than that of the wire (up to 50 times lower) and hence cannot be accurately known [24, 32]. In addition, it is also very difficult to measure the actual biomass reaction temperature.

In most of all these devices, the sample reaction occurs in transient conditions, leading to several difficulties in results interpretations.

The devices relying on ablative and radiant pyrolysis concepts allow to work in FP and steady state conditions with large biomass samples. In the first case, rods of wood are perpendicularly applied under pressure on a hot spinning disk [19]. The rate of reaction is derived from the direct measurement of rod consumption velocity. The experiments evidence the formation of intermediate liquid compounds. These former experiments have been at the origin of AP reactors. In the second case, the cross section of a biomass sample is submitted to a concentrated radiation (delivered by a xenon lamp associated to concentrating mirrors) [11, 12, 22, 23]. The imposed available heat flux densities can be quantitatively adjusted at will inside large ranges of values (roughly from 0.08 until 8 $MW \cdot m^{-2}$). The sample is settled inside a transparent quartz vessel fed by a cold (and not absorbing) gas in such a way that the primary species formed by pyrolysis are immediately quenched before further analysis. In the case of cellulose and under high flux densities, almost no char is formed. The mathematical modeling of the phenomena (providing assumption on physical constants) theoretically allows to derive reaction temperature [11, 12] and kinetic constants.

3.2 Continuous Reactors (used at both laboratory and pilot scales) [1, 2, 6]

They will be described without any preferential order.

3.2.1 Operations with Bubbling Fluid Beds (BFB)

Operations with Bubbling Fluid Beds (BFB) are widely carried out with throughputs from fractions of kg/h until several tons/h. A great number of works have been made for representing their thermal and hydrodynamic behaviours for which scaling laws are well established. Construction and operation are relatively simple. Efficient heat transfer exchanges occur between biomass and fluidizing solids (sand for example). Sizes of biomass samples should be adapted to the operating conditions: from a few millimeters until several cm according to BFB size. The measured temperature is relatively uniform and easily controllable. However it is a mean value of solid, biomass and gas phase temperatures. Hence, actual biomass pyrolysis temperature cannot be accurately known. In addition, because of the high temperature of the fluidizing gas, cracking reactions cannot be avoided in the bed nor in the freeboard. Fine particles are also entrained and may act as vapour cracking catalysts. The use of efficient gas/solid separators at the exit of the reactor is required. Combustion of reaction byproducts can be a source of heat for the reactor. A typical example is the Dynamotive process (up to 8 000 kg/h) [33].

3.2.2 Circulating Fluid Beds (CFB)

They have similar behaviours as BFB even if closer to transported beds. The solids (sand and char) are recovered and submitted to combustion in a secondary reactor providing recycled hot sand to the pyrolyser. Hot fluidizing gas uses also pyrolysis gas.

3.2.3 Rotating Cone

This original device invented by Twente University (NL) has given rise to a several hundred kg/h throughput process [34]. Biomass and sand particles are transported through centrifugal forces in a rotating cone and without the use of a gas. As in CFB, char is recovered and combusted in a separate reactor inside which recycled sand is reheated.

3.2.4 AP Reactors

They rely on the basic principle of heat transfer occuring through more or less direct contact between massive biomass samples and a hot moving surface. High contact pressure improves the reaction efficiency (see above). Several continuous reactors types have been designed. The rotating hot cylinder on which is pressed a biomass rod can be used for basic research [35]. In the rotating blade reactor, pressure and hot surface motion are derived mechanically [36]. In the PyTec process, the reactor relies on the hydraulical feeding of wood particles onto a rotating electrically heated surface [37]. This device is close to the most fundamental pioneering device using a hot spinning disk [19]. Among the advantages of AP reactors are the high contact heat transfer coefficients; the fast elimination of primary liquids from the hot zone; the fact that they operate with big size biomass samples (hence minimizing the cost of grinding); the possibility to use cold carrier gas (allowing the quenching of primary species). The hot surface may be treated for having catalytic effects.

In other types of systems, biomass particles are transported at high velocity and enter tangentially inside a hot walls reactor against which they move and undergo rapid heating and reaction. The reactor may be cylindrical as the NREL (formerly SERI) vortex reactor [38] or have the characteristics of a usual cyclone separator [39-41]. In that case, the solid byproducts are automatically separated at the bottom, while gases and vapours escape at the top. The bulk gas phase temperature may be lower than that of pyrolysis temperature and hence, once produced, the primary vapours are partially quenched inside the hot vessel itself. According to the walls temperature, it is possible to maximise vapours or gases production (multifunctional reactor). Throughputs as high as 1 kg/h can be reached in an only 0.5 L volume vessel.

In all these cases, high heat flux densities should be available and applied at the walls of the reactor.

3.2.5 Auger and Screw kilns [2, 6, 42]

In these devices, biomass is mechanically moved through an oxygen-free hot tube. Heat carriers (balls) can be also used. Heat transfers imply direct solid-solid contacts (as in AP). Conversely to the previous cases, these compact and continuous systems do not require carrier gas. They can operate under low temperature and with heterogeneous feedstocks. The char fraction can be used for producing a slurry (mixture with condensed vapours).

3.2.6 Heated Walls Vertical Reactors

FP can be also studied in heated walls vertical reactors where fine biomass particles are injected at the top [43, 44]. According to the cases, these particles fall or are transported by a carrier gas. Such devices are interesting because simulating several pilot plant reactors. The

actual biomass particles temperature cannot be accurately measured and (in spite of their small sizes), cannot be assumed equal to that of the surrounding. Temperature and velocity gradients can exist in the flow and the determination of residence times is difficult. Complete modeling of the reactor is needed. Finally, because of the heating of the gas, it may be difficult to distinguish the primary formed species from those issued from secondary thermal crackings making difficult the direct upscaling of some results.

3.2.7 Vacuum Pyrolysis

As soon as the 19th century, pioneering experiments have shown that higher yields of vapours are produced under vacuum [27]. Later on, these results have been often confirmed at the laboratory scales. The reason is that under low pressure, the vapours are quickly and efficiently removed from the hot zones hence minimizing secondary reactions. It has been also shown that the kinetic constant of intermediate liquid vaporization is much higher under low pressure [45]. High vapours yields are obtained even in these conditions of relatively low heat transfer efficiencies. These reactors can process large particles and operate under low temperature (723 K). Carrier gas is not required. The Pyrovac process [46], which is no more in operation, could process several T/h.

3.3 FP in Non Inert Surrounding Conditions

Many research efforts are made for producing best qualities BO in a single step, in the presence of a reactive gaseous medium or of catalysts, with the aim to prepare gasoline and diesel. However, no specific new types of FP reactors seem to have been proposed for these purposes.

3.3.1 Hydropyrolysis [2]

It is possible to reduce BO oxygen content by adding H_2 in the pyrolysis reactor (a fluid bed for example) with the objective to perform pyrolysis and hydrocracking in the same vessel. The system operates in the presence of a suitable metal catalyst. Pressure must be optimized in order to fulfill two contradictory requirements that should be optimized: low pressure in order to enhance vapours production (less char formation – see above) and high pressure in order to improve the hydrogenation reaction [2].

3.3.2 Integrated Catalytic Processes [2, 47]

In these extensively studied systems, FP and catalysis are combined in order to produce better qualities fuels. A difficulty is that these systems are less flexible and should work inside narrow operating conditions. For example catalyst-vapours reactions (deoxygenation) should be favoured and, in the same time, vapours thermal cracking minimized (need of low temperature operation). Catalysts should be choosen in order to prevent lower pyrolysis rate and decline of vapours yields. Their regeneration is a basic aspect of reactor design. To be noticed that catalytic pretreatments of biomass (for example by impregnation) have not the same effects than the same catalyst separately introduced inside the reactor. In the first case, the catalyst modifies the primary biomass pyrolysis, while in the second, it modifies secondary reactions underwent by vapours.

DISCUSSION - CONCLUSION

Nowadays, FP of biomass is mainly carried out for the preparation of BO obtained after condensation of vapours produced by biomass thermal decomposition. The optimization and scaling up of current FP processes, as well as improvement of BO yields and qualities come against several scientific challenges that should be overcome. The purpose of the paper has been restricted to the only level of the FP reactor. Other challenges exist also at each level of the process (from biomass pretreatment until effluents conditioning). Some of them are briefly listed at the end of this discussion.

1. Scientific challenges at the FP reactor level:
   - no clear and general criteria are currently available for defining the conditions required for FP and for comparing systems operating in different conditions. For example, biomass temperature and heating rate are inappropriate. Actually, these usually considered parameters depend on the reaction extent and location inside the biomass sample. They are extremely difficult to measure in FP conditions. The actual reaction temperature may be much lower than that of the heat source. Other criteria have been suggested in the present paper;
   - temperature and kinetic data can be mainly obtained through the mathematical modeling of biomass samples pyrolysis for which several levels of simplificated assumptions can be made. A central difficulty in the solving of the models is the bad knowledge of all the physical constants of all the phases (including the short life time intermediates) involved in the reactions;
   - the biomass sample apparent rate of reaction depends on several coupled elementary processes such as chemical kinetics and heat and mass transfer resistances. There is no actual consensus in the

literature for representing kinetic pathways and related kinetic constants that would be valid for any kind of biomass, nor for its main components (cellulose, hemicelluloses, lignin). Thermodynamic data related to all involved products (including inorganics) are also still badly known. All these uncertainties result from the very great number of biomass types, the badly known internal interactions, the major roles of inorganics and the rapidity of chemical processes. They result also from the great number of research types facilities, the various types of measured informations, the various ways of biomass heating (convection, radiation, solid-solid contacts). Because of the high variabilities of biomass feedstock properties, the establishment of improved robust laws representing biomass behaviour according to those of its main components is recommended;

- basic data often obtained in laboratory facilities conditions should be cautiously used for modeling pilot plants operating in other conditions. It is for example the case of TGA derived informations corresponding to slow pyrolysis, even if it is the only device where reaction temperature is accurately known. For example, the domains of reaction temperatures are much lower (up to 150 K differences) in TGA than in FP conditions. Consequently, if the complex kinetics mechanism includes several elementary chemical processes having different activation energies, the controlling chemical steps could be different in both cases;
- internal interactions with char can also cause a decrease of vapours fractions leaving the sample;
- once liberated inside the reactor gas phase, the more or less primary species can undergo further reactions leading also to lower yields of lesser BO qualities. The kinetics of these reactions are still badly known. The literature reports a lot of data which are mainly available for model compounds and less for biomass itself. The extent of these reactions depends on reactor temperature field as well as on the complex gas and solid phases residence times distributions;
- BO are obtained from the recovery of condensable species issued from the reactor. They include vapours and also aerosols that can result from partial gas phase condensations but also from the direct ejection out of the reacting biomass sample. The mechanism of aerosols formation would merit further research efforts having in mind that their composition (water and particles contents, nature of organics fractions) may be much different than that of condensed vapours;
- a great number of reactor types can be used for FP. They can operate in transient or in steady state conditions. Most of them rely on the basis of usual gas-solid reactors even if in FP, gas-solid interactions should be avoided. Search of new concepts of reactors adapted to the specific case of biomass FP is recommended (decomposition reaction of a solid giving rise to three phases; high compositions and sizes variabilities of the feedstocks, implying high reactor flexibilities; minimization of secondary gas phase or gas-solid reactions with efficient internal quenching; ability of high heat flux densities exchanges). The comparison of reactors efficiencies is difficult because of the diversity of their basic principles. They are often compared on the basis of maximum biomass throughput. However such a criterium is scientifically insufficient. Also temperature and heating rate are inappropriate. Other additional scientific criteria should be imagined. Finally, scaling up should result from the complete modeling of all the implied and coupled phenomena (at reactor and particles levels);
- for the reactor itself, other difficulties result from the need to use high temperature resistant materials. Their behaviours and interactions with pyrolysis reaction products and with biomass ashes is another concern (for example in high temperature operations where ashes can undergo partial melting, especially on the walls).

2. Main scientific challenges at other levels of FP processes

The following list does not consider resource availability, nor socio, energetic and economic aspects:

- upstream of the reactor: best knowledge of biomass (structure, internal interactions, localization and catalytic role of inorganics). Conception of on-line biomass analysis methods; models of biomass drying; adaptation of biomass to the high temperature reactor (water content; particle size; possible pretreatment, for example washing for removing ashes or conversely impregnation with specific catalysts; physical densification). Problems of injection according to biomass particles sizes and reactor pressure;
- downstream of the reactor: optimization of vapours quenching (one step or staged condensation); efficiency of separators (ashes, char particles, aerosols) at high or room temperature and operating in conditions preventing secondary (crackings, repolymerizations) reactions which are not yet clearly identified; conditions of BO storage (temperature, role of inorganics and char

particles); identification of the numerous BO components and stabilities; levels of impurities and toxicity standards; problems of liquids fractionation;

– improvement of BO properties [48]. BO has several drawbacks for a direct use as gasoline or Diesel. They include for example: high oxygen (35-40%) and water (15-30%) contents, relatively low HHV (around 17 MJ/kg), complex mixture of several hundred of different organic compounds, aging (possible partial repolymerizations), acidity (pH = 2.0-3.7), relative high viscosity, poor distillability (thermal instability of BO), inhomogeneity and phase separation, solids contents (inorganics, char). BO upgrading (taking into account the great number of BO types according to biomass) is hence required. They include for example: physical upgrading (filtration of very small particles) and catalytic upgrading for BO deoxygenation and refining, including mainly hydrotreating by catalytic reaction under H_2 [2, 6]. Many research works are carried out on model compounds and models mixtures expected to mimic BO. Unfortunately only few comparisons are made with actual very complex BO;
– whole process: establishment of relationships between structure, variability and reactivity of biomass, and required process selectivities and level of flexibilities; energetic, exergetic and life-cycle analysis; increase of heat transfers efficiencies (reactors, exchangers, fast quenching). Conception of short response times instruments for on line analysis and that are able to operate under conditions of high temperature, short residence times and low concentration species (solid particles, gas phase and impurities). Byproducts upgrading and recycling, catalyst reconditioning, etc.

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