

# FLASH PYROLYSIS OF BIOMASS SUBMITTED TO A CONCENTRATED RADIATION. APPLICATION TO THE STUDY OF THE PRIMARY STEPS OF CELLULOSE THERMAL DECOMPOSITION

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## ABSTRACT

Concentrated radiation and more specifically concentrated solar energy can be used to drive thermochemical processes. Several types of chemical systems can be considered, aiming at the production of chemical energy carriers or the processing of chemical commodities. The solar thermochemical conversion of carbonaceous materials is one of the most often suggested option. In addition, concentrated light can be also used as a very efficient laboratory device for studying basic kinetic pathways in very clean conditions, as for example the primary steps of the biomass thermal degradation. The present paper describes the first results of experiments where small samples of cellulose are submitted to short flashes of a concentrated radiation provided by an image furnace. The observation of the surface after the reaction, as well as the HPLC analysis of the products bring evidence that the reaction passes through the intermediate of short life time liquid species. Thanks to a mathematical model taking into account the heat transfer limitations, it is possible to derive kinetic data that are compared to the results of the literature. In addition to these chemical results, the paper points out the importance of the optical properties of cellulose with respect to the efficiency of the sunlight absorption.

## INTRODUCTION

Concentrated radiation can be used to drive endothermal chemical reactions under controllable and very clean conditions of high heat flux densities. It is for example the case with concentrated solar energy that can be obtained through different devices like solar towers, dish concentrators, solar furnaces, ... The available powers range from a few kW to several MW according to the facilities. The aim of the first part of this paper is to briefly mention the main different domains of solar chemical reactions presently studied all over the world mainly in the framework of the SolarPACES program (1). Special emphasis will be given to the conversion of carbonaceous materials like biomass. All these studies are made in the context of search of new sources of renewable energies for a futur optimal protection of environment. The second part of the paper will show that concentrated radiation (obtained from a solar simulator) can be also used for studying the fundamental aspects of biomass thermal degradation. First results concerning the primary steps of cellulose pyrolysis will be given and compared to mathematical models.

## SOLAR THERMOCHEMISTRY AND SOLAR THERMOCHEMICAL PROCESSES

The first aim of the activities developed all over the world is the production of energy carriers : solar energy is converted into chemical fuels which can be stored for long times and transported over long distances. In addition, solar energy can also assist in the processing of high temperature chemical commodities. Among the chemical systems which are the most extensively studied are :

- The solar reforming of natural gas with the production of syngas
- The solar thermochemical storage of solar energy relying on the dissociation of ammonia
- The solar thermal production of H<sub>2</sub>. This can be done through the direct and very high temperature splitting of water or through thermochemical cycles based for example on the dissociation of metal oxides (like ZnO).
- The solar processing of specific chemical commodities like fullerenes, nanomaterials, ...
- The solar thermochemical conversion of biomass attracts also much attention since many years for several reasons (2). There are many ways of biomass thermal upgrading : gasification ; slow and fast pyrolysis ; ... leading to a great number of possible interesting products (gases, charcoal, bio oils, ...) with many potential utilisations (fuels, electricity, chemicals, ...). The corresponding solar assisted processes bring the advantages to upgrade the totality of the biomass feedstock and to design 100 % renewable plants with no use of fossil fuels, O<sub>2</sub> or air (gasification). The emissions are reduced and respect the natural cycle of carbon.

All these processes cannot be developed with the only knowledge of the chemical systems involved. They need to optimize the solar reactor where they are driven. Among the problems to be solved are: to maintain clean the window through which the solar radiation enters into the reactor ; to adapt the reactor to the nature of the solar facility (vertical or horizontal axis ; at the

ground or at the top of a tower ; ...); to be able to operate in transient conditions ; ... In addition, the optical properties of the absorbing solid reactants must be well known. Some failures in solar biomass conversion can be explained by the fact that some of its components are not perfectly absorbing materials. It has been for example recently shown that cellulose may reflect up to 80 % of the incident radiation and that it behaves also as a semi transparent material, meaning that important fractions of the radiation may cross the sample without any absorption (3).

### **CONCENTRATED RADIATION: A TOOL FOR STUDYING THE FUNDAMENTALS OF BIOMASS PYROLYSIS.**

A very great number of papers have been and continue to be published in the field of biomass thermochemical conversion. The aim of many of them is to derive kinetic models. However, these models are often valid for the unique device where they have been determined. It is the reason why there still exist many disagreements and also controversies (4). For example, it is not well understood if the vapours formed in cellulose fast pyrolysis are formed directly from a solid phase or through intermediate "active" liquid species.

Concentrated radiations can be available in very clean conditions of very high heat flux densities and during well controlled times. The following section will show that these conditions can be favourably used for a better understanding of the primary steps of cellulose thermal degradation.

#### **Experimental measurements**

The concentrated radiation is provided by an image furnace reproducing, at the laboratory scale, the conditions of a solar furnace. Its principle has been previously described in details (5). It relies on the use of a high power Xenon lamp located at the first focus of a first elliptical mirror, the second focus of which being adjusted at the same location as the second focus of a second elliptical mirror. The image of the arc of the lamp is then formed at its first focus, where the chemical tests on cellulose samples are performed. The available flux can be adjusted through the use of several diaphragms. A system of pendulum allows also to irradiate the samples during known times (as low as a few milliseconds). The cellulose samples subjected to the flashes of light may be under the form of a thin layer deposited on a glass surface or of small pressed cylinders. In that case, the sample is settled inside a transparent glass vessel feeded by argon, at the exit of which is placed a glass wool filter trapping the aerosols and condensibles. Several measurements can be performed:

- Observation of the surface of the irradiated sample with a microscope, after the flash.
- Measurements of mass balances (mass loss of the sample and mass increase of the filter).
- Analysis by HPLC of the products remaining on the sample and trapped on the filter.
- Analysis of the gases leaving the filter by GC.

#### **Experimental results**

With available heat flux densities close to  $10^7 \text{ W m}^{-2}$ , a film of cellulose of  $450 \pm 50 \mu\text{m}$  thickness completely disappears in about one second. The reaction does not produce measurable quantities of char. No reaction is visible for flashes lower than about 0.2 second. For intermediate durations of the irradiation, it is possible to microscopically observe the surface of the sample after cooling: the fibrillar structure of initial cellulose has disappeared with blunting of the contours as during a phase change. In the same time, agglomerations occur with the formation of large networks. This behaviour precedes the formation of vapours for longer times of flashes. Undoubtedly, these observations show that gases and vapours are formed only after cellulose has passed through short life time liquid intermediate species. Notice that if these species are liquid at the reaction temperature, they are solid at room temperature. These solid products are 100 % water soluble.

In similar experimental conditions but with pressed pellets of cellulose, these same intermediate species are observed. After a given time of flash, steady state conditions are reached. They correspond to a constant superficial thickness of the layer of liquid species (a few hundred of microns) and in the same time, to a linear increase of the weight of the products trapped on the filter, as the flash time increases. These experiments do not produce noticeable fractions of char. The mass balances are verified with accuracies of about 80 %. The remaining fraction is probably due to untrapped vapours (probably water) and to the formation of light gases. Their analysis is under investigation by gas chromatography but their fraction seems to be very low (less than a few %). These last measurements are difficult because of the high dilution of the gases in argon and also of the very short duration of each experiment.

The HPLC analysis of the aqueous solution of the intermediate species as well as of the products trapped on the filter are also under investigation. They reveal the presence of relatively few peaks compared to the analysis of the more usual bio oils derived from flash pyrolysis. The composition of the intermediate species is independant of the time of flash. The products trapped on the filter have increasing fractions of low molecular masses products when the time of irradiation increases. Most of the known peaks correspond to molecules

(oligoanhydrosaccharides) resulting directly from the depolymerization of the cellulose polymer. The intermediate liquid species contain high fractions of molecules with degrees of polymerization higher than 3 while the trapped products contain noticeable fractions of levoglucosan and cellulosan mainly for long flash times experiments.

### Theoretical

In addition to these experiments it is possible to build models representing the thermal decomposition of cellulose. They rely on heat and mass balances at the level of a solid sample submitted to a given external available heat flux density and undergoing an endothermal chemical reaction occurring in competition with internal heat transfer resistances. The reaction is supposed to give rise to liquid species remaining on the sample and disappearing by a secondary reaction giving vapour species leaving the surface without any mass transfer resistance.

The model relying on the thin film experiences correspond to a first approximation to the so-called chemical regime : constant sample temperature (no gradient) and reaction controlled by chemistry. The phenomena occur in transient conditions. The pressed thick pellet experiments correspond to the so called ablation regime : after a short time, steady state conditions are reached the reaction occurring near and inside a thin superficial layer, while the heart of the pellet is at room temperature.

The agreement between these 2 models and the two different types of experiments is good, assuming that the rate constants for the 2 processes (cellulose  $\rightarrow$  intermediate species  $\rightarrow$  vapours) are those usually chosen in association with the Broido Shafizadeh kinetic pathway (4). However the comparison strongly depends upon the values of the thermophysical properties of cellulose and of the liquid species (thermal conductivity ; mass density ; heat capacity) as well as of their optical characteristics (emissivity ; absorptivity ; reflectivity) that will have to be more accurately measured in the future.

### CONCLUSION - DISCUSSION

Concentrated radiation (ex. concentrated solar energy) can be used to drive thermochemical reactions for the preparation of energy carriers and/or of chemical commodities. It is for example the case for the solar upgrading of biomass. The high qualities of a concentrated radiation can also be used as a laboratory tool for studying the primary steps of biomass thermal degradation. The experiments described have been favourably performed in very reproducible conditions with a solar simulator (image furnace) and with cellulose samples. They show that if it is well known that lignin passes through a liquid phase, it is also the case for cellulose. In spite of many previous experimental and theoretical evidences, this phenomenon continued to be questioned (4) and even rejected (6). The results presented in this paper show that in conditions of high heat flux densities, the existence of intermediate liquid species resulting from the partial depolymerization of cellulose cannot be ignored and that a simple model of the cellulose  $\rightarrow$  vapours type does not represent the reality. Notice that if these liquids play important and favorable roles in ablative pyrolysis (7,8) they can also create problems in entrained flow reactors where they can lead to agglomerations between the particles and finally increase the risks of clogging.

The liquid intermediate species observed in the present work can be compared to the "active cellulose" postulated in the Broido Shafizadeh model, even if these authors had few chances to observe a liquid phase during their low temperature experiments. Anyway, such a kinetic pathway associated to the often used and accepted rate constants allows to favourably predict our results. This agreement is observed thanks to mathematical models derived in the two extreme situations of the chemical and ablation regimes. However, our works show the necessity to better determine the thermophysical properties of cellulose and of its products of depolymerization.

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