



Review

Cellulose pyrolysis kinetics: An historical review on the existence and role of intermediate active cellulose

Jacques Lédé*

Laboratoire Réactions et Génie des Procédés, CNRS-Université de Lorraine, ENSIC, 1 rue Grandville, BP 20451, 54001 Nancy Cedex, France

ARTICLE INFO

Article history:

Received 9 November 2011

Accepted 22 December 2011

Available online 30 December 2011

Keywords:

Cellulose

Pyrolysis

Active cellulose

Kinetic models

Historical review

ABSTRACT

Cellulose pyrolysis, studied since more than one century, has been the object of a great number of papers. Several related kinetic models have been established in large experimental conditions, from slow to fast pyrolysis. Unfortunately, no actual consensus is reached. The primary formation of intermediate species accompanied or not with phase change phenomena are amongst the main matters of concerns. The purpose of the present review is to report the controversies, well-established knowledges and unresolved questions concerning the existence and role of intermediate species (often called “active cellulose”). After a general discussion, a few research topics are suggested at the end of the paper.

© 2012 Elsevier B.V. All rights reserved.

Contents

1. Introduction and purpose of the review	18
2. Brief historical considerations	18
2.1. Wood carbonisation and distillation	18
2.2. Cellulose pyrolysis	19
2.3. Provisional conclusions	19
3. First evidences of phase change phenomena during cellulose heating	19
4. First pyrolysis kinetic studies: from the 50s until the end of the 70s	19
5. New results published after Copper Mountain's meeting until the end of the 80s	21
6. New models and controversial papers published in the 90s	22
6.1. Controversial papers	23
6.2. New evidences of an initiation step	23
6.3. Models of cellulose particle pyrolysis	24
7. First detailed discussion in 1999 on the existence or not of an intermediate state in biomass pyrolysis [88,89]	25
7.1. Actual reaction temperature	25
7.2. Physical nature of the primary products	25
7.3. Chemical kinetics considerations	25
7.4. Chemical structure of the primary products	25
8. Last decade (2000 until now): new results, new models, new evidences for the existence of primary intermediate species	26
9. Discussions and conclusions	28
9.1. Kinetic models of cellulose pyrolysis	28
9.2. Discussions about IAC	28
9.2.1. Phase change phenomena	28
9.2.2. DP decrease (slow heating)	28
9.2.3. DP decrease (fast heating)	29
9.2.4. IAC properties	29

* Corresponding author. Tel.: +33 0 3 83 17 52 40; fax: +33 0 3 83 32 29 75.

E-mail address: Jacques.Lede@ensic.inpl-nancy.fr

9.2.5. Cellulose melting?	29
9.2.6. Practical interests of IAC	29
9.2.7. Chemical kinetics connected to IAC	29
9.3. Few recommended basic research topics and related difficulties	30
Acknowledgement	30
References	30

1. Introduction and purpose of the review

Since several millennia, biomass is considered as one of the major sources of energy, chemicals and materials as reminded by Antal and Gronli [1] in the framework of the specific case of charcoal production. The transformation of biomass can be performed either by biochemical or thermochemical routes. High temperature processes bring several advantages including the fact that all the main feedstock components (cellulose, lignin, hemicellulose) of any type of biomass can be upgraded. The great number of possible types of thermochemical processes differ according to the operating conditions, types of reactors and biomass, objectives, etc. They are usually classified into combustion, gasification and pyrolysis [2–4]. In combustion, biomass is burned under an excess of O₂ for energy generation. In gasification performed under lower O₂ fractions (or of steam) the aim is to maximise the production of gases for several possible applications: energy generation; H₂ or CH₄ preparation; production of synthetic biofuels, etc. Pyrolysis (carbonisation, distillation, pyrogasification, pyroliquefaction, slow or fast pyrolysis) is carried out under inert atmosphere with the production of various fractions of solids (charcoal), liquids (bio-oils, tars), gases. In all these thermal processes, the chemical phenomena begin with primary steps of biomass thermal decomposition followed by secondary reactions (crackings, gas phase-solid interactions, etc.). To be noticed that the same word “Pyrolysis” is used for describing either the elementary pyrolysis reactions or the whole pyrolysis process. The present paper relies on the more or less primary steps of biomass pyrolysis.

These chemical reactions are often in competition with heat and mass transfer phenomena and may also depend on the hydrodynamic characteristics of the reactor. Their relative importances depend on the experimental conditions. For example, a recent paper [4] describes the difficulties in the search of reliable criteria for defining required experimental conditions in the case of fast pyrolysis. The still bad knowledge of kinetic pathways and parameters of biomass primary pyrolysis are amongst the main difficulties. In spite of the great number (several hundred) of published papers, no consensus is presently reached in the literature. The discrepancies may result from the fact that different types of biomasses having different heterogeneous structures and properties are used. Also several published kinetic parameters may vary according to the laboratory device where they have been measured and hence, their use for modelling other operating conditions may be questioned. Other reasons include the difficulties in defining and measuring the actual biomass reaction temperature, the rapidity of chemical phenomena with resulting controls by transfer processes, etc.

Many published results have been obtained with cellulose, often considered as a model compound of biomass. Its mass fractions in biomass roughly range between 40% and 50% (on dry basis). Cellulose is a well known high molecular weight linear polymer of β-(1-4)-D-glucopyranose units linked together by (1-4)glycosidic bonds [5]. These repeating units are cellobiose units (two glucose units). Cellulose is of a crystalline nature with regions of amorphous structure. Its DP is highly variable and may reach several thousands. Groups of cellulose chains make microfibril sheets which are at the basis of complex fibres [5].

The purpose of the present paper is to review some of the main significant results published since more than 100 years in the field of cellulose thermal decomposition. Special attention is focussed on the problems connected to the existence, nature and role of intermediate species formed in the early moments of its degradation. Their formation, accompanied or not by phase change phenomena, continues to be an unresolved research topic giving rise to numerous discussions since several decades. It is not a simple academic debate. Actually, the existence and nature of such species can have more or less important impacts at different levels: interpretation of kinetic measurements, design of reactors, particles behaviours, preparation of new products, biomass combustion, fires, etc.

This review follows a chronology which is arbitrarily divided into several periods of times including:

- Brief historical considerations.
- First evidences of phase change phenomena during cellulose heating.
- First pyrolysis kinetic studies: from the 50s until the end of the 70s.
- New results published after Copper Mountain’s meeting until the end of the 80s.
- New models and controversial papers published in the 90s.
- First detailed discussion in 1999 on the existence or not of an intermediate state during biomass pyrolysis.
- Last decade (2000 until now): new results, new models, new evidences for the existence of primary intermediate species.

By the way, an other indirect purpose of the present paper is to show that interesting results have been already obtained several decades ago and that serious current interpretations should not ignore such pioneering works.

2. Brief historical considerations

2.1. Wood carbonisation and distillation

Wood thermal degradation is used by mankind since several thousand years and for a great number of applications. In his review on charcoal production, Antal and Gronli [1] report, for example, cave drawings dated 30 000–38 000 years BP and also its use for ore reduction. Greeks and Romans civilisations also extensively exploited Mediterranean forests woods for their industry (smelting works, glass making plants, etc. [6]). More quantitative works have been also published by Violette [7] in 1853 following a previous paper presented in 1851 [8] to the War Minister and Science Society Academy on the carbonisation of a great number of wood sample species. These works clearly point out the strong influence of experimental conditions on the properties of pyrolysis products. Another important work is reported in the “*Traité de Métallurgie*” by Gruner [9].

Wood pyrolysis liquids have been also recovered since a long time by very ancient oriental, Mediterranean and northern civilisations after separation of the charcoal out of the furnace. Their varied uses ranged, for example, from boats coatings, until corpse embalming (Egyptian Pharaohs civilisation). A great number of pioneering works performed in the 18th and 19th centuries show that

Download English Version:

<https://daneshyari.com/en/article/1197416>

Download Persian Version:

<https://daneshyari.com/article/1197416>

[Daneshyari.com](https://daneshyari.com)