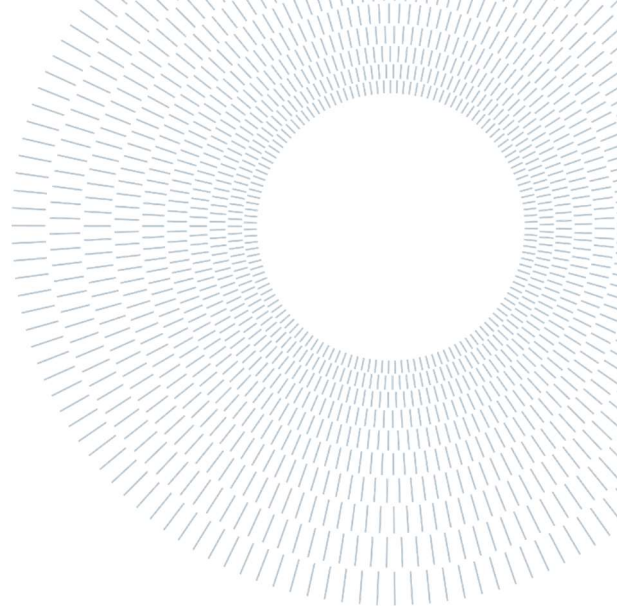




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EXECUTIVE SUMMARY OF THE THESIS

Thermal degradation of cellulose: upgrading of a semi-detailed kinetic model based on new experimental data

TESI MAGISTRALE IN CHEMICAL ENGINEERING – INGEGNERIA CHIMICA

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1. Introduction

While the world energy demand has increased over the last decades, fossil fuels still remain the main energy sources. However, their extensive use leads to environmental issues as the emissions of greenhouse gases and pollutants. Consequently, the worldwide countries are supporting the transition from a fossil fuel-dominated energy outlook to a more sustainable lower-carbon one. In such framework, biomass is a promising solution in order to replace fossil fuels. The present work only focuses on lignocellulosic biomasses because they do not compete with food supply chain. Given its high efficiency, the thermochemical conversion of lignocellulosic biomass is an attractive opportunity to produce valuable biofuels, biochemicals and biomaterials. In such domain, pyrolysis represents the most relevant alternative, since it is the first step involved also in combustion and gasification processes. However, the pyrolysis of lignocellulosic biomass is a complex problem, due to its multi-scale, multi-phase and multi-component inherent nature. In order to design efficient conversion technologies,

both experimental and numerical investigations are required. Such approach is very useful to propose accurate models able to describe the process features.

Lignocellulosic biomass is mainly composed by three constituents: cellulose, hemicellulose and lignin. Cellulose accounts for more than 50% of the dry weight in many feedstocks. The devolatilization of cellulose is characterized by the release of light gases and heavier tars, together with the formation of solid char.

Several models of cellulose pyrolysis have been proposed by a lot of authors in the past decades. In particular, the starting CRECK model [1] presents a semi-empirical approach, with an intermediate level of complexity and a semi-detailed characterization of products.

In order to properly investigate the kinetics, reliable data not affected by transport phenomena must be collected. Several experimental devices such as micro-pyrolyzers enable to neglect transport effects and ensure a kinetically limited regime.

Recent developments in analytical methods increased accuracy and number of detected species. More specifically, the LCCP group introduced a novel TGA-based set-up for pyrolysis

experiments, providing a complete quantitative speciation and kinetically informative data.

In this work, an improved kinetic model for the pyrolysis of cellulose is proposed. The upgraded model takes the previously available CRECK model of cellulose pyrolysis [1] as a starting point. Using TGA-based data, the kinetic scheme is refined, addressing both devolatilization trends and product distribution. The proposed model is further validated with literature data. For the sake of clarity, the starting model and the improved model are referred to as Model V20 and Model V23, respectively.

The work is organized as follows: the state-of-art on the kinetic study of cellulose pyrolysis is analyzed in Section 2. The materials and experimental methods are detailed in Section 3 together with a description of Model V20. Section 4 presents a comparison between experimental data collected in TGA-based set-up and Model V20 predictions. The improvements introduced in Model V23 are described in Section 5, showing the complete scheme of lumped species and reactions. Section 6 discusses the comparison of TGA data with the Model V23, while Section 7 deals with the validation of the model with additional data taken from the literature.

2. Kinetic study of cellulose pyrolysis: review of the state-of-the-art

The analysis on the kinetic study of cellulose pyrolysis comprises not only the description of analytical methods for kinetic experiments, but also the evolution of lumped and mechanistic models that describe the cellulose devolatilization. Thermogravimetric analyzers and micro-pyrolyzers are the most relevant experimental devices. While TGA provide mass loss and its derivative profiles, micro-pyrolyzers allow to guarantee short residence times and disregard secondary gas-phase reactions. Conversely, other experimental devices such as drop tube, entrained flow, hyperthermal nozzle or micro-fluidized bed reactors involve transport phenomena and, as a result, they are not able to provide a purely kinetic regime.

Over the past decades, several models of cellulose pyrolysis have been proposed by a lot of authors. Lumped and mechanistic models are two valid alternatives with a different level of detail,

complexity and flexibility. Comparing the two options, mechanistic models allow to involve a higher number of reactions and chemical species, but they are not flexible. Thus, considering cellulose as a reference species to characterize a generic biomass, lumped kinetic models enable to predict the yields of char, tars and light gases for a wide range of operating conditions and feedstock properties.

Among all the proposed models in literature, Ranzi et al. developed a semi-detailed kinetic mechanism, using a significant number of lumped species.

3. Materials and methods

3.1. Starting Model V20 of cellulose pyrolysis

In Model V20, cellulose decomposes to produce active cellulose (CELLA), which reduces the degree of polymerization without any release of volatile products. Then, active cellulose may decompose along two concurrent reactions. The former brings to the formation of levoglucosan (LVG), while the latter yields char, water and non-condensable gases such as hydroxy-acetone, glyoxal, acetone, hydroxyl-acetaldehyde and 5-hydroxy-methyl-furfural, together with lighter products such as formaldehyde, formic acid, CO and CO₂. Thus, the formation of LVG is predominant at temperatures lower than 750K with respect to the decomposition process, which prevails at higher temperatures according to a higher activation energy. In addition, in order to reproduce the concerted pathway with a set of sub-sequential reactions, a side charring exothermic reaction directly from cellulose is considered.

In order to simulate pyrolysis experiments, the cellulose kinetic Model V20 is integrated into a semi-batch reactor model, where the solid biomass undergoes devolatilization and pyrolysis vapours exit the reactor; simulations were performed in OpenSMOKE++, a numerical framework for numerical simulations of reacting systems.

3.2. Pyrolysis in a TGA-based set-up

A commercial microcrystalline cellulose is utilized for this study. The experiments are carried out in a novel TGA-based set-up, which allows to couple the tracking of mass loss curves with a

comprehensive quantitative product speciation. This set-up is developed by the LCCP research group. In particular, pyrolysis tests are run in a thermogravimetric analyzer where cellulose samples are subjected to a controlled heating rate from room temperature to 1073 K, under inert atmosphere (He). Using specific analytical techniques such as online MS and offline GC/MS-FID on liquid and vapour products, the entire product slate is characterized and quantitatively described. Thus, the integral mass yield of each species is determined. Such data are organized, analyzed and processed in the present work. In order to refine the semi-detailed kinetic model, a comparison between model predictions and TGA-based data are carried out in the following section.

4. Model V20 assessment using in-house experimental data

Model V20 kinetic scheme is used to simulate the TGA experiments, aiming to assess the model predictive accuracy. Fig. 1 compares LCCP experimental mass loss trends with model predictions. It is observed that the model predictions agree quite well with the mass loss trends and solid residual, even if a slight delay at higher temperatures for all the heating ramps exists. Discrepancies can also be observed in the last 20-30% of mass loss, especially at the high heating rates, where the model does not enable to capture the decrease of reactivity.

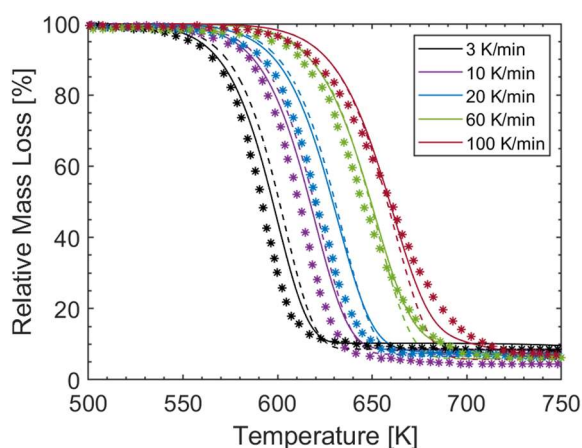


Figure 1. Mass loss curves at varying heating rates. Scatters = experimental data; dashed lines = Model V20; solid lines = Model V23.

Fig. 2 shows the comparison between Model V20 predictions and the LCCP data at 100 K/min for different classes of products, including sugars,

furans, light oxygenates, H₂O, light gases (CO, CO₂) and char residue. While the model captures general trends (e.g. the predominance of levoglucosan, the limited yields of char and light gases), a significant discrepancy emerges on underpredictions of sugars yield, and overpredictions of light oxygenates and light gases yields. In particular, the model overpredicts the formation of CO, CO₂ and C₂ and C₃ organic compounds from primary pyrolysis. Furthermore, the experiments allow to better identify the pyrolysis products with respect to the model; for instance, species C₄, C₅ and C₇ are observed experimentally, but absent in the model.

On the basis of such evidence, the starting model is refined. The proposed modifications are described in the following section.

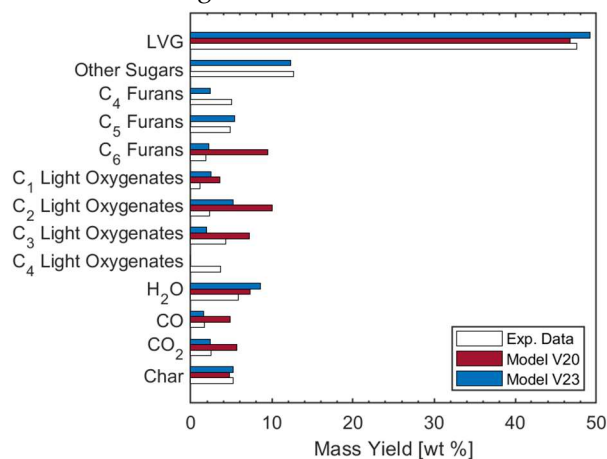


Figure 2. Comparison between the LCCP data and the predictions of the two models at 100 K/min in terms of product distribution.

5. Updating the kinetic scheme

As a result of the new experimental findings, the refined Model V23 includes new reactions and lumped species, as outlined in Table 1.

The framework of Model V23 is analogous to that of Model V20, involving a first depolymerization step (R1) of cellulose (CELL) and producing active cellulose (CELL_A). Notably, in the new Model V23, this reaction presents a lower activation energy of 45 kcal/mol (compared to 47 kcal/mol in Model V20), aiming to anticipate the initial devolatilization stage at lower temperatures in order to follow the experimental mass loss curves reported in Fig. 1. Similarly to Model V20, CELL_A may decompose along two competitive reactions: the decomposition (R3) to anhydrosugars and the fragmentation (R2) to lighter products, water, light

gases and char. However, these two reactions are enhanced with a partial de-lumping of the species. Differently from Model V20 that considered LVG as the only lumped species for all the sugars, a new pseudo-species $C_6H_{10}O_5$ is introduced in order to predict the formation of other anhydrosugars besides levoglucosan. Additionally, metaplastic levoglucosan G{LVG} is introduced in order to capture the decrease of reactivity observed within the last 20-30% of mass loss curves, attributed to its delayed release. Two release reactions, R9 (with a lower activation energy) and R10 (with a higher activation energy), are inserted to differentiate between low and high heating rates behaviors. Furthermore, new lumped species as FURAN and FURFURAL are introduced among the decomposition products in reaction R3, representing respectively a C_4 and C_5 species, which were absent in Model V20.

In addition to species partial de-lumping, related to the new experimental findings, the kinetic parameters of reaction R2 are modified in order to increase the sugars yields at the expense of light oxygenates.

Lastly, a side dehydration and charring exothermic reaction (R4) directly from CELL is considered, similarly to Model V20. Its pre-exponential factor is increased in order to guarantee a greater yield of char.

In the next section, the Model V23 of cellulose pyrolysis is compared with the LCCP data in order to highlight the effectiveness of the proposed modifications on both thermal degradation and product distribution of cellulose with respect to Model V20.

6. Model V23 assessment using in-house experimental data

Modified Model V23 predictions have been compared with TGA-based data in Fig. 1 and Fig. 2, in terms of devolatilization trends and product distribution, respectively. Differently from Model V20, the refined Model V23 allows to better reproduce the experimental mass loss curves, not only anticipating the initial degradation, but also capturing a decrease of reactivity in the final devolatilization stage. More specifically, the inclusion of the metaplastic species G{LVG} and its delayed release result in a more accurate description of the high temperature trends.

The model ability of matching the product distribution are substantially improved. Due to changes in reactions R2 and R3, and consequently, their ratio R3/R2, sugars yields are increased at the expense of light oxygenates, getting closer to experimental results. In addition, the partial de-lumping of condensable products leads to a more detailed depiction of pyrolysis products. In contrast to the original model, the modified mechanism satisfactorily aligns with experimental data, including furans and light oxygenates well distributed in the C_4 - C_6 and C_1 - C_3 range, respectively. Furthermore, the new pseudo-species $C_6H_{10}O_5$ comprises all the experimentally observed sugars that are not LVG.

Table 1. Improved kinetic mechanism of cellulose pyrolysis (Model V23).

| Kinetic Mechanism | | | Kinetic Parameters |
|-------------------|---------------------------------------|---|--|
| | | | A [1/s], E_{act} [kcal/kmol] |
| R1 | CELL | → CELL _A | $7.00 \cdot 10^{13} \cdot \exp(-45000/(RT))$ |
| R2 | CELL _A | → 0.026 CH ₂ OHCH ₂ CHO + 0.3705 CH ₂ OHCHO + 0.036 CHOCHO + 0.049 CH ₃ CHO + 0.088 C ₆ H ₆ O ₃ + 0.1657 CH ₃ OH + 0.1058 CH ₂ O + 0.1595 CO + 0.28 CO ₂ + 0.204 H ₂ + 1.5007 H ₂ O + 0.162 HCOOH + 0.0371 CH ₄ + 0.901 CHAR + 0.07 G{CO} + 0.05 G{COH ₂ } _{Loose} + 0.024 G{H ₂ } + 0.18 FURAN + 0.1323 CH ₃ COCH ₃ + 0.287 FURFURAL | $8.50 \cdot 10^5 \cdot \exp(-19100/(RT))$ |
| R3 | CELL _A | → 0.6 LVG + 0.2 G{LVG} + 0.2 C ₆ H ₁₀ O ₅ | $6.92 \cdot 10^4 \cdot \exp(-15000/(RT))$ |
| R4 | CELL | → 0.125 H ₂ + 4.45 H ₂ O + 5.45 CHAR + 0.125 G{H ₂ } + 0.12 G{COH ₂ } _{Stiff} + 0.25 G{CO} + 0.18 G{COH ₂ } _{Loose} | $8.00 \cdot 10^7 \cdot \exp(-31000/(RT))$ |
| R5 | G{CO} | → CO | $5.00 \cdot 10^{12} \cdot \exp(-52500/(RT))$ |
| R6 | G{COH ₂ } _{Loose} | → 0.2 CO + 0.2 H ₂ + 0.8 H ₂ O + 0.8 CHAR | $6.00 \cdot 10^{10} \cdot \exp(-50000/(RT))$ |
| R7 | G{COH ₂ } _{Stiff} | → 0.8 CO + 0.8 H ₂ + 0.2 H ₂ O + 0.2 CHAR | $1.00 \cdot 10^9 \cdot \exp(-59000/(RT))$ |
| R8 | G{H ₂ } | → H ₂ | $1.80 \cdot 10^8 \cdot \exp(-70000/(RT))$ |
| R9 | G{LVG} | → LVG | $9.50 \cdot 10^{-2} \cdot T \cdot \exp(-10000/(RT))$ |
| R10 | G{LVG} | → LVG | $6.00 \cdot 10^{11} \cdot \exp(-45000/(RT))$ |

7. Validation of Model V23 on the basis of literature data

In order to ensure a validity of the updated cellulose pyrolysis mechanism across a wide range of operating conditions, the validation procedure involves a comprehensive comparison between the model predictions and experimental data taken from the literature.

The validation procedure first takes into examination mass loss curves, as depicted in Fig. 3. Such comparison is extended across a large window of heating rates, including slow (10-20 K/min [2]), fast (100-1000 K/min [3][4]) and flash (100 K/s and 1000 K/s [5]) pyrolysis conditions.

When compared to Model V20, Model V23 shows an improved agreement with experimental data not only confined to the range of slow heating rates considered for model refinement, but also extended convincingly to fast and flash pyrolysis cases.

Notably, the inclusion of metaplastic levoglucosan and its delayed release, described by reactions R9 and R10, significantly enhance the model capability to accurately describe the experimental trends and the decrease in reactivity in the final stage of degradation.

After the validation in terms of devolatilization trends, an assessment on the efficacy of the model in terms of product distribution is carried out. For this purpose, Model V23 is compared with experimental data taken from the literature [6-11].

Such datasets are obtained by isothermal pyrolysis experiments on several commercial cellulose samples (microcrystalline and non-crystalline) and in a temperature range of 673K-873K.

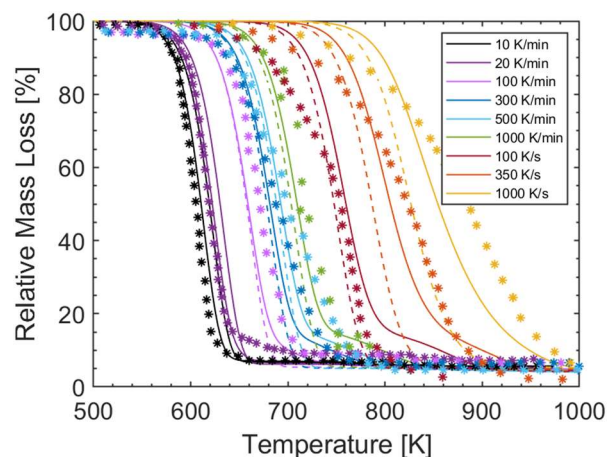


Figure 3. Mass loss curves at varying heating rates. Scatters = experimental data; dashed lines = Model V20; solid lines = Model V23.

As illustrated in Fig. 4, measured and calculated mass yields of different classes of products - levoglucosan, furans, light oxygenates, water, char and light gases - have been compared.

Notably, there is a visible variability among the experimental data; hence, the model aims to find a balance in its predictions. Fig. 4A shows an improved ability of Model V23 in predicting the LVG production. Refined LVG yields are higher than those of Model V20 (e.g., at 773K: 42.8% for Model V23 vs 27.48% for Model V20), but still

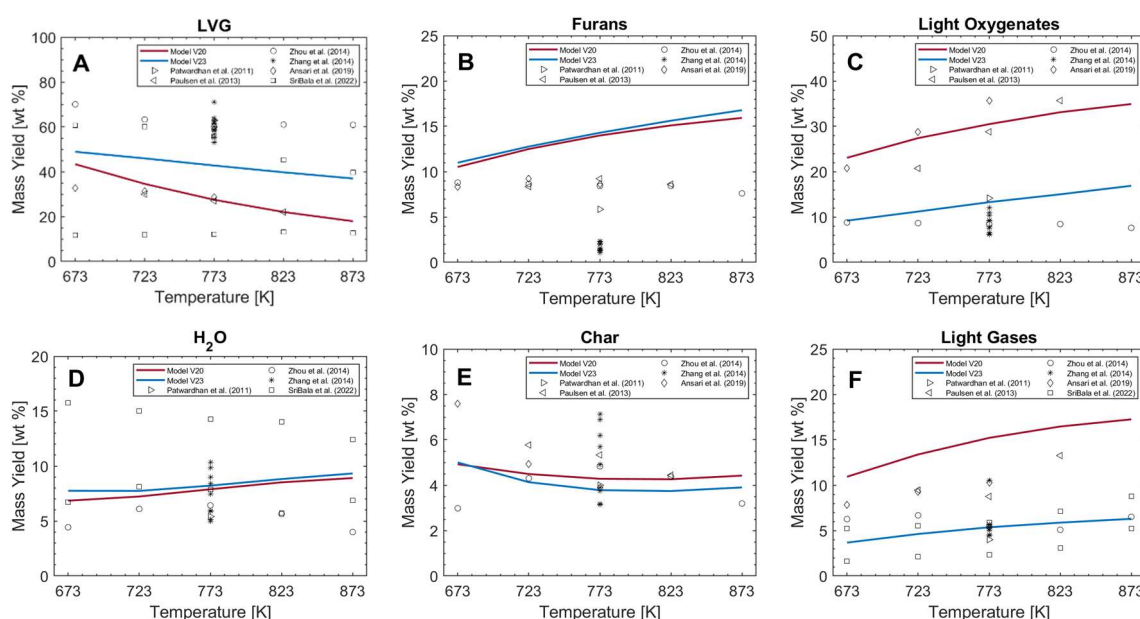


Figure 4. Comparison between model predictions and experimental data from the literature in terms of mass yields: (A) LVG, (B) Furans, (C) Light Oxygenates, (D) H₂O, (E) Char, (F) Light Gases.

lower than the majority of literature data (e.g. between 55 and 70% at 773K). Fig. 4B reports the measured and predicted mass yields of furans at different temperatures. In such case, Model V23 has a similar trend to the previous version. However, both models overestimate the production of furans. Such evidence, combined with the insights from LVG, suggests that pyrolysis at high heating rates tends to form less furans and more sugars when compared to that at low heating rates in TGA. Fig. 4C proves that the Model V23 predictions in terms of light oxygenates production agree with the majority of literature data. As displayed in Fig. 4D-E, predictions of H₂O and char yields well align with experimental trends. Lastly, Fig. 4F demonstrates a remarkable enhancement in the Model V23 predictions of light gases (CO and CO₂), since they were previously overestimated.

8. Conclusions

In the present work an updated semi-detailed kinetic model of cellulose pyrolysis has been proposed. Exploiting experimental data collected in a novel TGA set-up, the model has been refined. It enables to predict the formation and release of 13 oxygenated hydrocarbons such as anhydrosugars, furans, aldehydes, alcohols, ketones and carboxylic acids. The upgraded model has been further validated with literature data collected in micro-pyrolyzers set-ups. The modified model has shown satisfying results not only in reproducing mass loss trends for slow, fast and flash pyrolysis conditions, but also in predicting both the distribution of volatiles. Moreover, the modification of kinetic parameters and the partial de-lumping of species have improved the model predictive ability in terms of C₆ anhydrosugars, C₄-C₆ furans and C₁-C₃ light oxygenates. While the comparison of Model V23 predictions with literature data allows to validate the efficacy of the model at high heating rates, the scarcity of complete speciation data from TGA experiments in the existing literature limits the model validation at low heating rates. Further improvements can be related to the inclusion of secondary effects, such as the influence of degree of polymerization and crystallinity index on both the devolatilization trends and product distribution.

9. References

- [1] P.E.A. Debiagi et al., "Kinetic Modeling of Solid, Liquid and Gas Biofuel Formation from Biomass Pyrolysis", *Biofuels and Biorefineries*, vol. 10, pp. 31-76, 2020.
- [2] Gao, Z. et al., "Comparative study on the pyrolysis of cellulose and its model compounds". *Fuel Process Technol.*, vol. 193, pp. 131-140, 2019.
- [3] Y. Qiao et al., "Thermal decomposition of castor oil, corn starch, soy protein, lignin, xylan, and cellulose during fast pyrolysis", *Bioresour. Technol.*, vol. 278, pp. 287-295, 2019.
- [4] I. Milosavljevic and E.M. Suuberg, "Cellulose thermal decomposition kinetics: global mass loss kinetics", *Ind. Eng. Chem. Res.*, vol. 34, pp. 1081-1091, 1995.
- [5] M.R. Hajallogol et al., "Product compositions and kinetics for rapid pyrolysis of cellulose", *Ind. Eng. Chem., Prod. Res. Dev.*, vol. 21, no. 3, pp. 457-465, 1982.
- [6] P.R. Patwardhan et al., "Distinguishing primary and secondary reactions of cellulose pyrolysis", *Bioresource Technol*, vol. 102, no. 8, pp. 5265-5269, 2011.
- [7] A.D. Paulsen et al., "The Role of Sample Dimension and Temperature in Cellulose Pyrolysis", *Energy Fuels*, vol. 27, no.4, pp. 2126-2134, 2013.
- [8] X. Zhou et al., "Experimental and Mechanistic Modeling of Fast Pyrolysis of Neat Glucose-Based Carbohydrates. 1. Experiments and Development of a Detailed Mechanistic Model", *Ind. Eng. Chem. Res.*, vol. 53, no. 34, pp. 13274-13289, 2014.
- [9] J. Zhang et al., "Investigation of Primary Reactions and Secondary Effects from the Pyrolysis of Different Celluloses", *ACS Engineering Au*, vol. 2, pp. 2820-2830, 2014.
- [10] K.B. Ansari et al., "Fast Pyrolysis of Cellulose, Hemicellulose, and Lignin: Effect of Operating Temperature on Bio-oil Yield and Composition and Insights into the Intrinsic Pyrolysis Chemistry", *Ind. Eng. Chem. Res.*, vol. 58, pp. 15838-15852, 2019.
- [11] G. SriBala et al., "New Perspectives into Cellulose Fast Pyrolysis Kinetics Using a PyGC × GC-FID/MS System", *ACS Engineering Au*, vol. 2, pp. 320-332, 2022.