

Development of a lumped kinetic model for the ex-situ biomass catalytic pyrolysis

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Highlights

- 1st order lumped kinetics are assessed within thermal pyrolysis & catalytic upgrading
- The effect of C/B ratio and temperature are incorporated in the kinetic analysis
- Catalyst deactivation is evaluated under a time-dependent function

1. Introduction

Among the various aspects that can be met in the processing of lignocellulosic biomass through fast pyrolysis (e.g. catalyst evaluation, operating conditions, reactor configuration), the evaluation of kinetics that are involved in thermal pyrolysis and subsequent catalytic upgrading of pyrolysis vapours, receives significant research attention [1]. While a group of literature studies rely on the use of model compounds [2], the concept of a lumped-reaction scheme is considered simplified, yet more flexible during the evaluation of process scale-up and optimization of reaction conditions [3]. To this end, the present study analyzes the kinetic modeling results that have been verified within an ex-situ biomass catalytic pyrolysis process and under a proposed lumped reaction scheme incorporating catalyst deactivation.

2. Methods

Figure 1a presents the pyrolysis pilot-scale unit of the Laboratory of Environmental Fuels & Hydrocarbons (CPERI/CERTH) that was used for the kinetic model validation. Lignocellulosic biomass is fed to the first unit reactor (thermal pyrolysis) and through a fluidization medium (N₂) and high heating rates, pyrolysis vapours are sequentially entering the catalytic reactor. Under the presence of a ZSM-5 based catalyst, upgrading of the vapours in terms of oxygen removal takes place and bio-oil (organic phase) is being collected after rapid condensation of the exit stream.

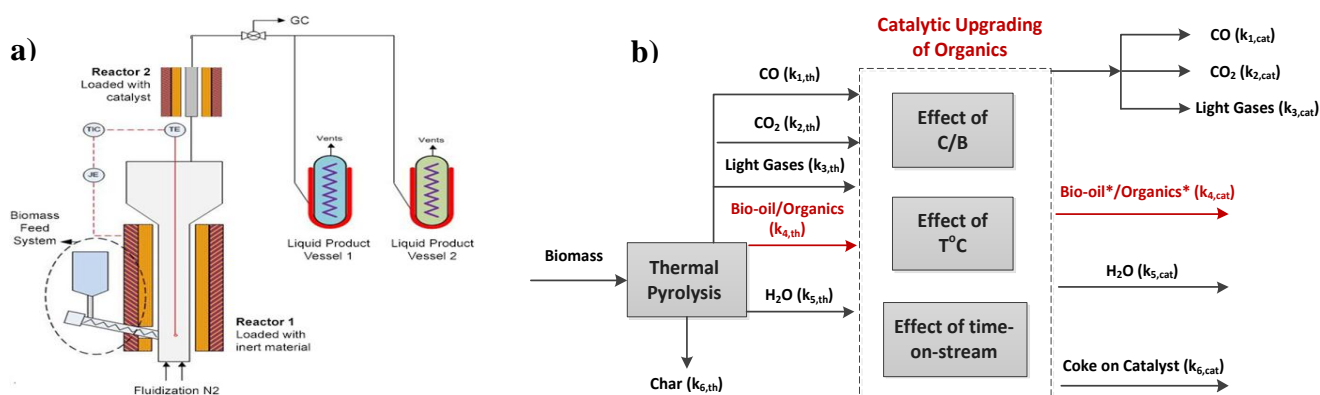


Figure 1. a) Biomass ex-situ catalytic pyrolysis unit at LEFH/CPERI, b) extended lumped-reaction kinetic scheme for both stages

On the same trend, Fig. 1b highlights the proposed lumped reaction kinetic scheme for this process. As can be seen, during thermal pyrolysis, biomass is decomposed into gases (CO, CO₂ and light gases up to C₆), condensable liquids (bio-oil and water) and solid (char). From all components that enter the second unit

reactor (except char), organics/thermal bio-oil under a similar lumped reaction scheme are being upgraded towards a bio-oil product of significantly lower oxygen content. Core aim of the proposed methodology is to kinetically evaluate the effect of a) catalyst/biomass (C/B) ratios (0.15-0.5), b) operating temperature for the catalytic upgrading stage (450-600°C) and c) time-on-stream (10-60min) that could predict yields under the applied operating conditions and enhance unit scaling-up. The following equations evaluate the kinetic rates of the respective lumps as presented in Fig.1b [4]:

$$\frac{dw_{i,th}}{d\tau} = r_{i,th} = k_{i,th} \cdot w_{biomass} \quad (\text{lumps } i = \text{biomass, CO, CO}_2, \text{LightGases, Organics, H}_2\text{O, Char})$$

$$\frac{dw_{i,cat}}{d\tau} = r_{i,cat} = k_{i,cat} \cdot w_{organics} \cdot \alpha(t) \quad (\text{lumps } i = \text{CO, CO}_2, \text{LightGases, Organics*H}_2\text{O, Coke})$$

$$\frac{d\alpha}{dt} = f(t)$$

where $r_{i,th/cat}$ denote the reaction lump rate at thermal/catalytic stage in min^{-1} for lump i ($k_{i,th/cat}$ refers to the Arrhenius kinetic parameter), $w_{biomass/organics}$ the mass fraction of biomass/organics in % at the respective feed stage, $w_{i,th/cat}$ the i^{th} lump mass fraction at thermal/catalytic pyrolysis in %, τ reactor residence time in min and $\alpha(t)$ time-dependent deactivation rate.

3. Results and discussion

An overview of recent kinetic modeling results has been presented in a previous study by the authors and for a constant operating temperature [4]. Initially and regarding thermal pyrolysis stage, literature kinetic parameters were finely tuned and the output data from thermal pyrolysis kinetics were utilized as input data towards the kinetic evaluation of the catalytic upgrading. As has been found, the increase of C/B ratio (\sim denoting reactor residence time) significantly promotes oxygen removal in the form of CO, CO₂ and H₂O, under the expense however of a lower bio-oil/organics mass yield. Coke formation was also increased at higher C/B ratios as a consequence of higher hydrocarbon cracking rates. On the other hand, the effect of increased time-on-stream was detrimental to the process due to the enhanced coke formation. Specifically, through the course of time, coke was deposited on the ZSM5-based catalyst and gradually blocked sites that are responsible for bio-oil oxygen removal. Hence, oxygen content in bio-oil increased significantly (\sim 30% from 25min to 60min) that ultimately lead to a product of low processing value (high acidity, higher heating value, etc.).

4. Conclusions

Ultimate aim of this study is the development and verification of a flexible kinetic modeling strategy that will be able to predict product yields under different operating conditions for biomass catalytic (ex-situ) pyrolysis. As has been found, the applied lumped reaction scheme can fit accurately the experimental data under different residence time and under the progressing effect of coke formation with time (catalyst deactivation), predicting lumped mass yields (gas, liquid, solid) with an overall statistical error <10%.

References

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Keywords

Biomass pyrolysis; kinetic modeling; catalyst deactivation; low oxygen bio-oil