
Fundamental Understanding of Co-(Fast)-Pyrolysis of Biomass and Polymers for Energy and Resource Recovery

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Abstract

The generation of drop-in fuels and intermediates from lignocellulosic biomass via fast pyrolysis is a promising strategy for large-scale production and utilization of biofuels. However, bio-oil produced via catalytic pyrolysis of biomass contains significant oxygen that excess hydrogen is required for the upgradation of bio-oil in the downstream operation. The main focus of this work is to investigate if the presence of thermoplastic polymers would improve the hydrogen content in bio-oil. In this work, reaction kinetics of co-pyrolysis of cellulose and polypropylene (PP) of different compositions under low ($5\text{ }^{\circ}\text{C min}^{-1}$) to medium heating rates ($180\text{ }^{\circ}\text{C min}^{-1}$) in a thermogravimetric analyzer, and very high heating rates ($> 2000\text{ }^{\circ}\text{C s}^{-1}$) in a micropyrolyzer are studied. Weight loss profiles and differential thermograms were analyzed using various conventional techniques like Freidmann method, Chang method, Kissinger method, Flynn-Wall-Ozawa technique and Coats-Redfern plots to evaluate the rate parameters, viz. activation energy (E_a) and frequency factor (A), and reaction order (n) at various stages of conversion. The products of fast pyrolysis were analyzed in a GC/MS to understand the key interactions between cellulose and PP under rapid heating rate conditions. All these information were utilized to develop a predictive kinetic model of decomposition of cellulose + PP involving the key reaction steps like (i) formation of active cellulose, levoglucosan and char, (ii) formation of vapor phase species from PP, and (iii) interaction of PP vapors with char formed from cellulose. The model predictions and useful mechanistic insights on the key interactions between cellulose and PP will be discussed in this presentation.

Keywords: *Co-pyrolysis, fast pyrolysis, cellulose, polypropylene, kinetics*

1. Introduction

Biomass is a precious resource for the production of bio-oils and an efficient substituent of petroleum based oils. First-generation biofuels were produced from starch crops, but the usage of food crops and environmental impacts were the cause of concern. The present generation biofuel production focuses on utilizing high-yielding non-food crops such as lignocellulosic biomass for increasing the yield of bio-oils, reducing their environmental impacts and economics involved.

Thermochemical processing employs application of heat and catalyst to convert diverse biomass feedstocks to fuel. (Fast) pyrolysis is a potential thermochemical route for the large scale production of bio-oils and useful intermediates. It involves decomposition of organic matter in the absence of oxygen at moderate temperatures ($400\text{--}600\text{ }^{\circ}\text{C}$) under very short time scales (milliseconds to a few seconds).^[1]

Bio-oils must be upgraded to reduce the oxygen and ash content for its application as a fuel intermediate /blend-stock. Conventional upgradation by hydrodeoxygenation requires significant amounts of hydrogen to remove oxygen in bio-oil as H_2O or CO_2 . In this regard, co-pyrolysis of biomass with thermoplastic polymers would be a cost effective solution. The decomposition of cellulose, a major component of biomass, proceeds by a network of concerted

reactions,^[2] while commercial PP degrades via a free radical mechanism.^[3] In the combined system, it is highly probable that hydrogen abstraction reactions between polypropylene and cellulose aid in improving the overall H-content in bio-oil.^[4] This significantly brings down the downstream processing costs.

The key focus of this work is to understand the kinetics of slow and fast co-pyrolysis of cellulose and polypropylene by thermogravimetric analysis (TGA) and micropyrolysis experiments, respectively, and develop a kinetic model to describe the key step of mass loss and rate limitations.

2. Materials and Methods

Microcrystalline cellulose ($50\text{ }\mu\text{m}$) and polypropylene (PP; $M_n = 3,700$, $M_w = 14,000$) were procured from Sigma Aldrich. Individual and mixed samples of cellulose and PP of c.a. 10 mg were heated from ambient to $900\text{ }^{\circ}\text{C}$ in SDT Q600 TGA (TA Instruments) under N_2 flow of 100 mL min^{-1} . Fast pyrolysis of the samples was carried out in a Frontier 3030 single-shot micropyrolyzer (Frontier-Lab, Japan) in the temperature range of 350 to $500\text{ }^{\circ}\text{C}$. Rapid pyrolysis of c.a. $500\text{ }\mu\text{g}$ of the sample was achieved at a rate of $>2000\text{ }^{\circ}\text{C s}^{-1}$ in a few seconds. The pyrolyzed vapors were analyzed in a Shimadzu 2010 gas chromatography/mass spectrometer (GC/MS). A HP-5ms column was utilized to separate the components, which were quantified using a flame ionization detector.

3. Results and Discussion

3.1 Co-pyrolysis in TGA

Cellulose and PP in weight ratios of 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100 were pyrolyzed in TGA at various heating rates, viz., 5, 10, 20, 50, 100 and 180 °C min⁻¹. The thermogram exhibited two distinct peaks corresponding to the decomposition of cellulose and PP. Cellulose and PP decomposed in the temperature ranges of 300 – 380 °C and 400 – 500 °C, respectively. A detailed kinetic analysis of weight loss profiles were performed using the conventional techniques of Friedmann, Kissinger, Chang, Flynn-Wall-Ozawa and Coats-Redfern.^[5] The apparent activation energies (E_a) of thermal decomposition of the mixtures were evaluated and it was found that E_a of cellulose decomposition was unaffected by the presence of PP (< 3 kcal mol⁻¹ variation), while the presence of cellulose greatly enhanced the degradation of PP. Figure 1 depicts the variation of E_a evaluated by the first Kissinger technique, which is based on maximum rate of weight loss of the sample at various heating rates.

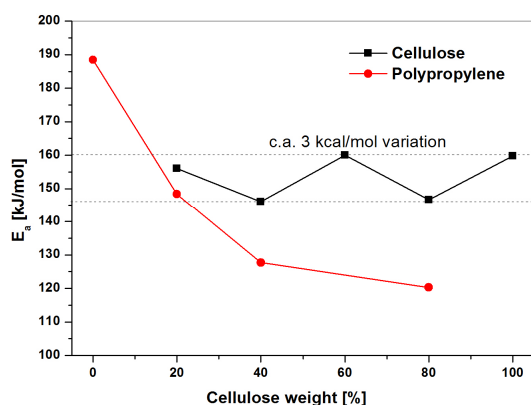


Figure 1. Variation of E_a of cellulose and PP with composition according to first Kissinger technique.

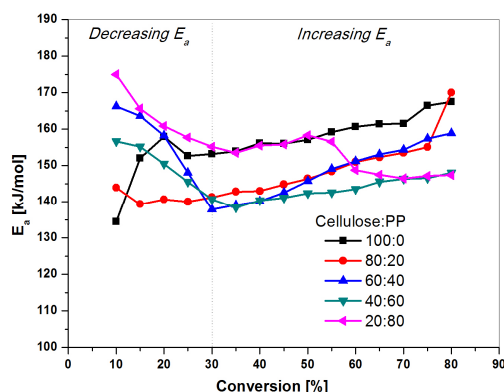


Figure 2. Variation of E_a with conversion according to Flynn-Wall-Ozawa method.

Flynn-Wall-Ozawa method was utilized to investigate the variation of E_a with conversion at heating rates, and as shown in Figure 2, it is clear that there is a significant increase in E_a of almost all the mixtures after a total conversion of 30 wt.%. This shows that char, that is

initially formed as a result of cellulose pyrolysis, aids in cracking the primary pyrolysis vapors from PP to form secondary gas phase species. All these information were utilized in building a combined kinetic and transport model of co-pyrolysis of cellulose and PP, that can eventually be extended to biomass + polymer system. Currently, a completely segregated model is found to satisfactorily describe the experimental weight loss profiles. However, the inclusion of key interactions in the model are underway to comprehensively describe the mechanism.

3.2 Co-pyrolysis in Micropyrolyzer

Fast co-pyrolysis of cellulose and PP is currently being investigated in a micropyrolyzer-GC/MS system to understand the nature of interactions under high heating rate conditions. In this regard we are monitoring the change in product composition as result of inclusion of polymer in biomass. Apart from individual product yields, we are also studying various properties of bio-oil like elemental composition, acid value, molecular weight and high heating value. The interesting features of this part of the study and a comparison of the mechanism of co-pyrolysis under slow and fast pyrolysis conditions will be discussed in the presentation.

4. Conclusions

In this work, we have studied the co-pyrolysis behavior of cellulose and PP as a mimic to understand the behavior of biomass and thermoplastic polymers under such reaction conditions. The TGA analysis shows a clear interaction between cellulose and PP, which is reflected in lower E_a of PP decomposition in presence of cellulose. Currently, micropyrolyzer studies under fast pyrolysis conditions and modeling activity are underway to understand the product distribution in bio-oil and the controlling mechanism under various reaction conditions.

References

- [1] Brown, R.C. (Ed). In: *Thermochemical Processing of Biomass Conversion into Fuels, Chemicals and Power*, 1st Ed.; UK (2011) Wiley.
- [2] Vinu, R.; Broadbelt, L. J. *Energy Environ. Sci.* 5 (2012), 9808-9826.
- [3] Kruse, T. M.; Wong, H.-W.; Broadbelt, L. J.; *Macromolecules.* 36 (2003) 9594-9607.
- [4] Pérez, M.G.; Chaala, A.; Yang, J.; Roy, C. *Fuel* 80 (2001) 1245-1258.
- [5] Wang, X.-S.; Li, X.-G.; Yan, D. *J. Appl. Polym. Sci.* 78 (2000) 2025-2036.