



# Understanding the Interactions Between Cellulose and Polypropylene During Fast Co-Pyrolysis via Experiments and DFT Calculations

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Co-pyrolysis of lignocellulosic biomass with waste plastics is a promising option to produce high quality liquid fuels. During co-pyrolysis the molecular level interactions between the intermediates produced from biomass with polymers play a crucial role in altering the distribution of various organics in bio-oil. Recently, it was shown that interactions between cellulose and polypropylene during fast co-pyrolysis leads to the formation of C8-C20 long chain alcohols in bio-oil. The formation of alcohols was proposed to occur via reaction of hydroxyl radicals from cellulose pyrolysis with polypropylene radicals. This study is an attempt to unravel the formation mechanism of long chain alcohols during co-pyrolysis using quantum chemical calculations. The reactions of propylene trimer (2,4,6-trimethyl heptane) and its primary, secondary and tertiary radicals with hydroxyl radical ( $\bullet\text{OH}$ ) and water molecule are investigated at B3LYP/6-31G(d,p) level of theory using Gaussian 09. The reaction of  $\bullet\text{OH}$  with propylene trimer readily leads to the formation propylene trimer radicals with the liberation of water. The Arrhenius activation energy of this reaction is in the range of 11-14 kcal/mol. It is shown that the reaction of propylene trimer radical (primary, secondary or tertiary) with a water molecule readily leads to the formation of respective alcohols with Arrhenius activation energy of 10-14 kcal/mol. This reaction competes with the barrierless recombination of polypropylene radical with  $\bullet\text{OH}$ . However, the presence of  $\bullet\text{OH}$  is limited by the high reaction barrier for its abstraction from cellulose. Therefore, the reaction of polypropylene radicals with water molecules formed via cellulose dehydration is shown to be a plausible pathway for the formation of long chain alcohols during fast co-pyrolysis of cellulose and polypropylene. The mass loss profiles during fast co-pyrolysis for different cellulose:polypropylene compositions were obtained in a Pyroprobe® reactor. The first order rate constants of decomposition were evaluated, and they follow the order:  $0.044 \text{ s}^{-1}$  (cellulose:polypropylene 100:0) >  $0.041 \text{ s}^{-1}$  (75:25)  $\approx$   $0.042 \text{ s}^{-1}$  (50:50) >  $0.032 \text{ s}^{-1}$  (25:75) >  $0.028 \text{ s}^{-1}$  (0:100).

## 1. Introduction

Fast pyrolysis is one of the emerging technologies for the production of liquid fuels and platform chemicals from biomass. Fast pyrolysis involves rapid heating ( $>1000 \text{ }^\circ\text{C/s}$ ) of the biomass to moderate temperatures of 400-600  $^\circ\text{C}$  in inert atmosphere. The bio-oil yield is usually 60-75 wt.%, based on the biomass source and operating conditions (Vanderbosch and Prins, 2010). One of the major drawbacks of the bio-oil that limits its direct use in engines is its high oxygen content. This property imparts low storage stability, low calorific value, high viscosity and high acidity to bio-oil compared to conventional fuels. Therefore, bio-oil needs to be upgraded to high quality liquid fuel via catalytic hydrodeoxygenation, which requires high amount of hydrogen. Recently, co-pyrolysis of biomass with hydrogen-rich polyolefins such as polyethylene, polypropylene and polystyrene is seen as a promising strategy to improve the quality of bio-oil in the initial pyrolysis step. A number of studies have shown that the yield of bio-oil is improved during co-pyrolysis owing to the hydrogen transfer reactions between polyolefins and biomass radicals (Jakab et al., 2001; Sharypov et al., 2002, 2003; Pinto et al., 2015; Ojha and Vinu, 2015). Moreover, catalytic fast co-pyrolysis of biomass and polymers is

shown to produce high yield of aromatic hydrocarbons like toluene, ethyl benzene, xylenes, naphthalene and methyl naphthalene (Dorado et al., 2014).

Degradation of biomass components like cellulose and hemicellulose involve a number of condensed phase reactions like retro-aldol, retro-Diels Alder, dehydration and depropagation (Zhou et al., 2014), while the decomposition of polymers involve a number of free radical reactions like chain fission, propagation ( $\beta$ -scission, radical addition, inter- and intramolecular H-abstraction) and termination (Kruse et al. 2003). During co-pyrolysis, molecular level interactions between biomass and polymer free radical intermediates are envisaged, which lead to low concentration of oxygen in the bio-oil. Suriapparao et al. (2014) showed that the apparent activation energies of pyrolysis of mixtures of cellulose and polypropylene are lower (31-35 kcal/mol) than that of polypropylene (49 kcal/mol) and cellulose (38 kcal/mol). Recently, Ojha and Vinu (2015) evaluated the reaction time scale involved in fast co-pyrolysis of cellulose and polypropylene using Pyroprobe® reactor interfaced with Fourier transform infrared spectrometer (FT-IR). Figure 1 depicts the evolution of FT-IR spectra of the vapour phase when equal composition mixture of cellulose and polypropylene was fast pyrolyzed at 500 °C. It is evident that the maximum production of linear chain hydrocarbons, CO<sub>2</sub>, primary alcohols and carbonyl compounds occurs in 10-12 s. Importantly, the formation of long chain alcohols (C8-C20), which are not observed in cellulose pyrolysis, are observed as a result of interaction. The pyrolysis reaction time scale analysis also showed that co-pyrolysis leads to a shorter reaction time.

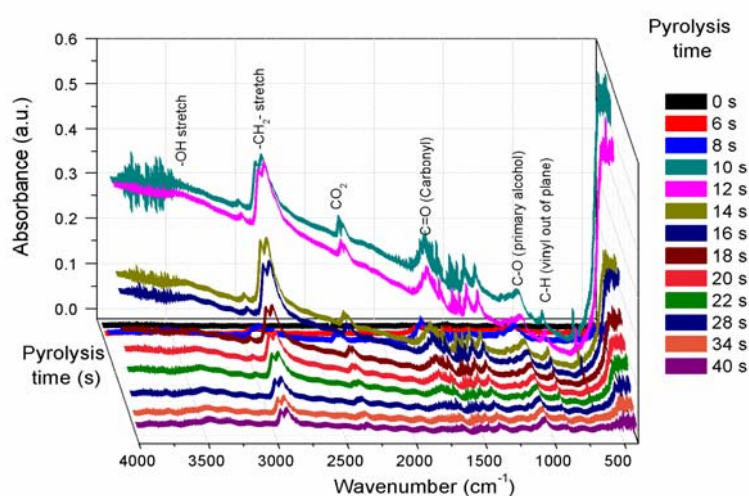


Figure 1: FT-IR spectra of vapor generated from 50:50 mixture of cellulose:polypropylene at 500 °C at different time instances (redrawn from Ojha and Vinu, 2015).

The objectives of the present study are two fold. Firstly, to experimentally determine the overall mass loss profiles during fast co-pyrolysis of cellulose and polypropylene at 500 °C, and evaluate the rate constants for different compositions. Secondly, to unravel the mechanism of formation of linear chain alcohols by studying the specific reactions of propylene trimer with hydroxyl radicals and water molecule using quantum chemical calculations.

## 2. Experimental and Computational Methods

Microcrystalline cellulose (50  $\mu$ m,  $M_n$  = 135,554 g/mol, polydispersity = 2.25) and polypropylene ( $M_n$  = 3,700 g/mol,  $M_w$  = 14,000 g/mol) were procured from Sigma Aldrich. Cellulose and polypropylene were thoroughly mixed in a mortar prior to pyrolysis. Fast co-pyrolysis experiments were performed in a Pyroprobe® 5150 pyrolyzer (CDS Analytical, U.S.A) equipped with a Brill cell. The samples were heated for two hours at 80 °C to remove the physical moisture before subjecting to pyrolysis. The brill cell interface was maintained at 200 °C and ultra pure N<sub>2</sub> was passed at a flow rate of 110 mL/min. Further details of the experimental set-up are provided elsewhere (Ojha and Vinu, 2015). 2 mg of the mixture was taken in the quartz tube and subjected to fast pyrolysis at 500 °C at a heating rate of 20 °C/ms. Mass loss data for different cellulose:polypropylene mixtures, viz. 100:0, 75:25, 50:50, 25:75 and 0:100, were collected by performing experiments for different holding periods from 2 to 50 s. All the experiments were repeated thrice and the standard deviation in every data point is reported.

In order to understand the interactions of polypropylene with hydroxyl radicals and water molecules during pyrolysis, density functional theory (DFT) calculations were performed in Gaussian 09 software package (2009). 2,4,6-Trimethyl heptane (propylene trimer) was chosen as the model compound of polypropylene, and

glucose as the model compound of cellulose. The functional used was B3LYP (Becke three-parameter Lee\_Yang\_Parr) (Becke, 1988, 1996; Lee et al., 1988), and 6-31G(d,p) was the basis set used to optimize the geometries of the reactants, transition states and products. B3LYP/6-31G(d,p) functional is earlier shown to estimate the transition states geometries more accurately for hydrogen abstraction and radical recombination reactions as compared to other more expensive basis sets (Sayes and Marin, 2003). Harmonic vibration and zero-point energy calculations were performed at the same level of theory. All minima were ensured to have zero imaginary frequencies while all transition state geometries were confirmed to have a single imaginary vibrational frequency. In order to match the transition state with the correct reaction, the intrinsic reaction coordinates, which connect the local minima of reactants and products, were followed in both the directions. Rate constant of reactions were calculated at 10K intervals in the temperature range of 500K-1000K using transition state theory. This computational study includes the thermochemical parameters, energies, geometries of reactants and products, and kinetics of specific reactions of propylene trimer and its primary, secondary and tertiary radicals with hydroxyl radical and water molecule.

### 3. Results and Discussion

#### 3.1 Kinetics of Fast Co-pyrolysis

Figure 2(a) depicts the mass loss profiles in the time range of 0 to 50 s. It is worthwhile to note that each data point was obtained by performing separate experiment for different holding periods. It is evident that cellulose exhibits faster decomposition compared to polypropylene, which is in agreement with the apparent activation energies evaluated by first Kissinger and Kissinger-Akahira-Sunose methods (Suriapparao et al., 2014). First order kinetic analysis of decomposition of the mixtures was performed by plotting  $\ln(w_0/w)$  vs pyrolysis time, where  $w_0$  and  $w$  are the initial mass and mass of sample at time  $t$ , respectively. The first order rate constant was evaluated from the slope of the linear plot. It is evident from Figure 2(b) that the regression coefficients for all the first order plots were greater than 0.985, which confirms the validity of first order kinetics. Other reactions orders like 1.5 and 2 resulted in poor fits with experimental data. The variation of first order rate constant,  $k$ , at 500 °C follows the trend:  $0.044 \text{ s}^{-1}$  (cellulose:polypropylene 100:0) >  $0.041 \text{ s}^{-1}$  (75:25)  $\approx$   $0.042 \text{ s}^{-1}$  (50:50) >  $0.032 \text{ s}^{-1}$  (25:75) >  $0.028 \text{ s}^{-1}$  (0:100). This shows that pyrolysis of cellulose-polypropylene mixtures results in faster overall degradation besides improving the quality of pyrolysis vapors in terms of long chain hydrocarbons and alcohols.

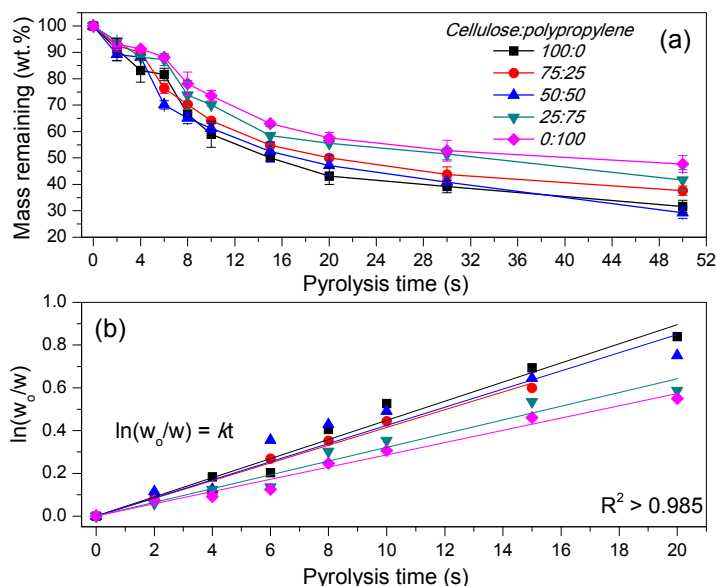


Figure 2: (a) Mass loss profiles for fast co-pyrolysis of cellulose-polypropylene mixtures of different compositions at 500 °C. (b) First order kinetic plots for the decomposition of cellulose-polypropylene mixtures.

#### 3.2 Density Functional Studies of Interaction of Cellulose and Polypropylene

In order to understand the melt phase interactions of polypropylene with cellulose pyrolysis products, the following reactions were investigated using quantum chemistry calculations in this study: (i) propylene trimer

with hydroxyl radicals, (ii) recombination of hydroxyl radicals with alkyl radicals, (iii) alkyl radicals with water molecule, and (iv) formation of  $\bullet\text{OH}$  from glucose.

Figure 3(a) depicts the reactions investigated in this study. Hydroxyl radicals can abstract hydrogen from primary, secondary or tertiary carbon atoms of the propylene trimer to form the corresponding free radicals and a water molecule. These reactions proceed via transition states, **TS1**, **TS2** and **TS3**. The primary (structure **2**), secondary (**3**) and tertiary (**4**) hydrocarbon free radicals can undergo barrierless recombination with  $\bullet\text{OH}$  to form the corresponding alcohols (structures **5**, **6** and **7**). However, in an alternate pathway, the hydrocarbon free radicals can also react with water molecules formed via dehydration of cellulose to form primary (structure **V**), secondary (**VI**) and tertiary (**VII**) alcohols via transition states, **TS4**, **TS5** and **TS6**, respectively, along with the formation of a  $\bullet\text{H}$  radical. The optimized geometries of all the transition state structures are presented in Figure 4.

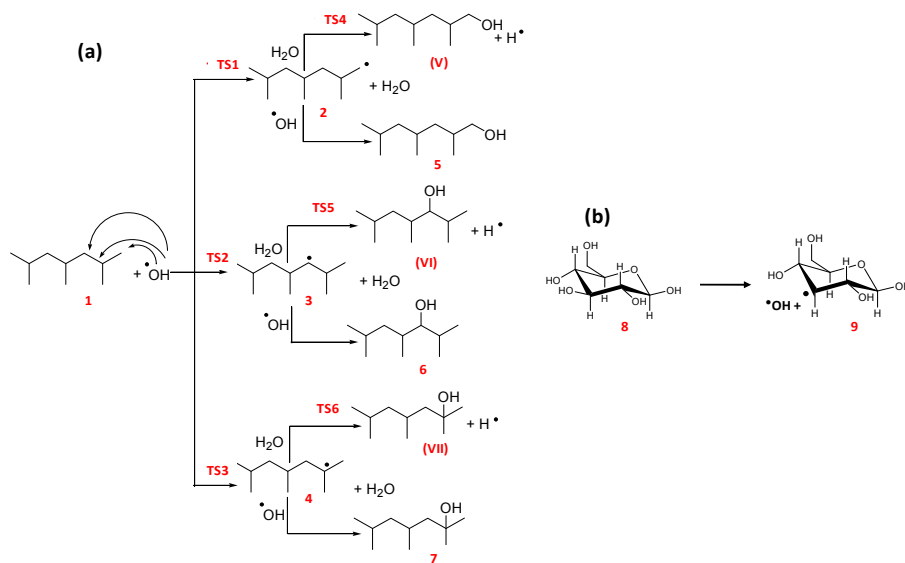


Figure 3: (a) Reactions of propylene trimer,  $\bullet\text{OH}$  and  $\text{H}_2\text{O}$  during fast pyrolysis of cellulose and polypropylene. (b) Dissociation of  $\bullet\text{OH}$  from the 3rd carbon atom of the glucose unit.

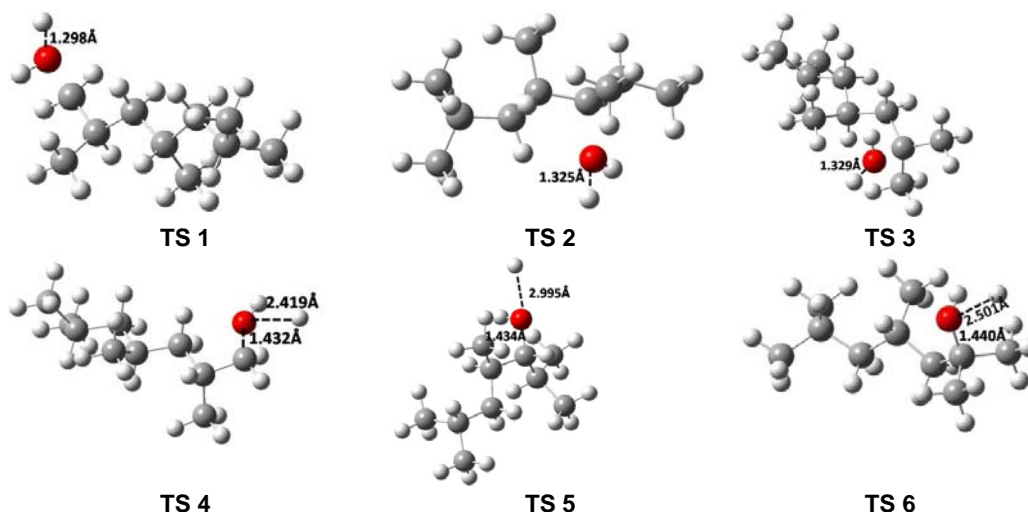


Figure 4: Optimized geometries of transition states involved in the interaction of propylene trimer with  $\bullet\text{OH}$  and propylene trimer radicals with  $\text{H}_2\text{O}$  during fast pyrolysis of cellulose and polypropylene calculated at B3LYP/6-31G(d,p).

Tables 1 and 2 provide the standard enthalpy change, Gibbs free energy change and entropy change associated with the various intermediates, products and transition state structures involved in the mechanism. From Table 2 it is clear that the formation of primary, secondary and tertiary hydrocarbon free radicals involve

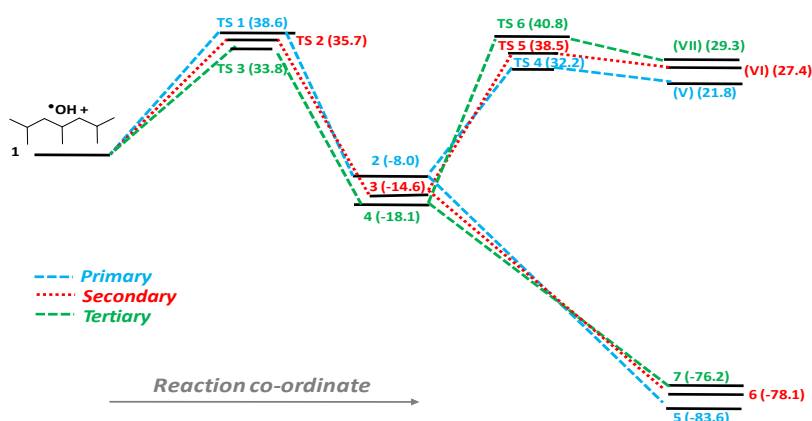
activation energies of 13.8, 12.3 and 11.4 kcal/mol, respectively, which is in agreement with the order of stability of these free radicals. Interestingly, the formation of alcohols via recombination of  $\bullet\text{OH}$  with various hydrocarbon radicals follows the trend: primary ( $\Delta G^\circ = -83.6$  kcal/mol) < secondary ( $-78.1$  kcal/mol) < tertiary ( $-76.2$  kcal/mol) (Figure 5). This shows that the formation of primary alcohol is highly probable when recombination of  $\bullet\text{OH}$  with hydrocarbon radical is the reaction mechanism. In the alternate pathway involving the reaction of hydrocarbon radicals with water molecule, the same trend in activation energy for the formation of alcohol is observed: primary ( $E_a = 10.3$  kcal/mol) < secondary (13.1 kcal/mol)  $\approx$  tertiary (13.8 kcal/mol) (Figure 5). This explains the formation of primary alcohols like 11-methyldodecan-1-ol, 2-hexyl-1-dodecanol, 3,7,11-trimethyl-1-dodecanol, 2-butyl-1-octanol, 2-hexyl-1-octanol, 2-hexyl-1-decanol and 2-isopropyl-5-methyl-1-heptanol in fast co-pyrolysis experiments (Ojha and Vinu, 2015).

**Table 1: Reaction enthalpy [ $\Delta H^\circ(25^\circ\text{C})$  kcal/mol], Gibbs free energy [ $\Delta G^\circ(25^\circ\text{C})$  kcal/mol] and entropy of reaction [ $\Delta S^\circ(25^\circ\text{C})$  cal/mol/K], calculated at B3LYP/6-31G(d,p)**

Reaction	$\Delta H^\circ$	$\Delta G^\circ$	$\Delta S^\circ$
1 $\rightarrow$ 2+H <sub>2</sub> O	-13.9	-8.0	-19.7
1 $\rightarrow$ 3+H <sub>2</sub> O	-21.0	-14.6	-21.7
1 $\rightarrow$ 4+H <sub>2</sub> O	-21.4	-18.1	-10.8
2+ $\bullet\text{OH}\rightarrow$ 5	-87.8	-83.6	-14.0
3+ $\bullet\text{OH}\rightarrow$ 6	-82.2	-78.1	-13.9
4+ $\bullet\text{OH}\rightarrow$ 7	-83.8	-76.2	-25.7
2 $\rightarrow$ (V)+ $\bullet\text{H}$	25.0	21.8	-16.5
3 $\rightarrow$ (VI)+ $\bullet\text{H}$	30.7	27.4	-20.1
4 $\rightarrow$ (VII)+ $\bullet\text{H}$	29.1	29.3	-19.9
8 $\rightarrow$ 9+ $\bullet\text{OH}$	93.3	80.6	-1.28

**Table 2: Transition state  $\Delta H^\ddagger(25^\circ\text{C})$  [kcal/mol], transition state  $\Delta G^\ddagger(25^\circ\text{C})$  [kcal/mol] and transition state  $\Delta S^\ddagger(25^\circ\text{C})$  [cal/mol/K] calculated at B3LYP/6-31G(d,p). Activation energy [ $E_a$ , kcal/mol] and pre-exponential factor [ $A$ , cm<sup>3</sup>/mol/s] were evaluated using the Arrhenius equation.**

	$\Delta H^\ddagger$	$\Delta G^\ddagger$	$\Delta S^\ddagger$	$E_a$	$A$
TS 1	29.6	38.6	-30.4	13.8	$4.2 \times 10^{-13}$
TS 2	26.1	35.7	-32.3	12.3	$1.6 \times 10^{-13}$
TS 3	24.0	33.8	-32.7	11.4	$1.3 \times 10^{-13}$
TS 4	21.9	32.2	-34.6	10.3	$5.1 \times 10^{-14}$
TS 5	26.9	38.5	-39.1	13.1	$5.4 \times 10^{-14}$
TS 6	28.1	40.8	-42.6	13.8	$9.1 \times 10^{-16}$



**Figure 5: Potential energy profile for reactants, intermediates, transition states and products involved in the interaction of propylene trimer with  $\bullet\text{OH}$  and H<sub>2</sub>O. Numbers denote Gibbs free energies in kcal/mol.**

The formation of hydrocarbon free radicals via  $\bullet\text{OH}$  radical pathway, as discussed in this work, competes with well known polymer pyrolysis reactions like chain fission, H-abstraction,  $\beta$ -scission and intramolecular backbiting reactions (Kruse et al., 2003). However, the formation of  $\bullet\text{OH}$  radicals in the system can occur only by thermolysis of cellulose, wherein the -OH group attached to 2nd, 3rd and 6th carbon atoms of the monomeric unit of cellulose are cleaved. The energetics associated with the cleavage of  $\bullet\text{OH}$  from the third position of a glucose unit was evaluated using B3LYP/6-31G(d,p) level of theory, and the reaction is shown in Figure 3(b). It is evident that the heat of reaction is 93.3 kcal/mol (Table 1), which indicates that the formation of  $\bullet\text{OH}$  from cellulose involves a very high energy barrier compared to dehydration of cellulose and glucose, whose activation energy lies in the range of 50-60 kcal/mol (Zhou et al., 2014). Therefore, it can be concluded that although the recombination of  $\bullet\text{OH}$  with polypropylene free radicals is a barrierless reaction, the formation of  $\bullet\text{OH}$  from cellulose is an energy intensive step. The plausible pathway for the formation of alcohols during

co-pyrolysis of cellulose and polypropylene can be attributed to the reaction of polypropylene free radicals with water of dehydration via transition state complex with activation energy in the range of 10-14 kcal/mol.

#### 4. Conclusions

In this manuscript, we have shown that cellulose-polypropylene mixtures decompose at a higher rate than polypropylene during fast co-pyrolysis. The first order rate constants followed the trend:  $0.044 \text{ s}^{-1}$  (cellulose) >  $0.041 \text{ s}^{-1}$  (75:25)  $\approx$   $0.042 \text{ s}^{-1}$  (50:50) >  $0.032 \text{ s}^{-1}$  (25:75) >  $0.028 \text{ s}^{-1}$  (polypropylene). The specific reactions, including (i)  $\bullet\text{OH}$  with propylene trimer, (ii) recombination of  $\bullet\text{OH}$  with propylene trimer radicals, (iii)  $\text{H}_2\text{O}$  with propylene trimer radicals, and (iv) formation of  $\bullet\text{OH}$  from cellulose, were studied using quantum chemical calculations. Owing to the high energy barrier involved in the formation of  $\bullet\text{OH}$  from cellulose (> 93 kcal/mol), recombination pathway is least preferred, while the one involving the reaction of water from cellulose dehydration with propylene trimer radicals is highly preferred. The variation of Arrhenius activation energy (in kcal/mol) follows the trend: primary alcohol (10.3) < secondary alcohol (13.1)  $\approx$  tertiary alcohol (13.8).

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