



Research paper

Kinetics of softwood kraft lignin inert and oxidative thermolysis

Samira Lotfi^{a,*}, Roozbeh Mollaabbasi^b, Gregory S. Patience^a^a Department of Chemical Engineering, Polytechnique Montréal, C.P. 6079, Succ. CV Montréal, H3C 3A7 Québec, Canada^b Department of Chemical Engineering, Laval University, 2325, rue de l'Université, Québec, G1V 0A6, Québec, Canada

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ABSTRACT

Oxidative and inert lignin thermolysis generate methane, CO, CO₂, and char but also intermediate valuable compounds. These thermos-sensitive compounds may either repolymerize or react further to light gases and char. Here, we characterized the lignin degradation kinetics versus temperature in a micro-fluidized bed reactor operating up to 870 K in nitrogen and air and measured product selectivity. The liquid yield during pyrolysis and oxidative thermolysis reached ~20% (predominantly aromatics). In the latter tests, oxygen reacted with lignin and mainly formed CO, CO₂, and CH₄ while in an inert atmosphere char was the principal product. We also monitored the mass loss of lignin in a thermogravimetric analyzer at heating rates of 5 K min⁻¹ to 30 K min⁻¹ (0.08 Ks⁻¹ - 0.33 Ks⁻¹). The heating rate dramatically affected the degradation of lignin in the oxidative thermolysis process. A two-step model characterized the lignin degradation behavior in both oxidative and inert lignin thermolysis. During lignin thermolysis; first, the weak bonds broke and char and gas formed. The remaining lignin depolymerized and reacted to aromatics and char. Lignin conversion, liquid yield and selectivity depended on the temperature. The activation energy between 600 K to 850 K was 47 kJ mol⁻¹ and it was 95 kJ mol⁻¹ at ~560 K. The pre-exponential factor varied with heating rate that indicated lignin degradation is limited by heat and mass transfer. The activation energy of lignin oxidative thermolysis at first step was lower compared to pyrolysis (40 kJ mol⁻¹) but considerably higher (200 kJ mol⁻¹) in the second step.

1. Introduction

Lignocellulosic materials are a source of fuels and a potential alternative to petroleum for chemicals. Lignin is a three dimensional amorphous polymer that link hydroxylated, methoxylated and phenylpropene units [1] and its composition and physico-chemical properties vary with the pretreatment methods include physical pretreatment (i.e., ball milling), solvent fractionation, chemical pretreatment (acidic, alkaline, and oxidative), and biological treatment (using predominately fungi) and plant [2,3]. Lignin has been largely failed as a chemical feedstock but is an attractive alternative to petroleum as constitutes up to 40% of the lignocellulose and is the only source of aromatics from biomass [1,2,4]. The lignin market is limited to low value products such as fuels, dispersing and binding agents (2% of lignin). The US Department of Energy recommends that bio-refineries concentrate on converting lignin to selective products rather than thermal processes like pyrolysis, gasification, liquefaction and combustion. Yield and selectivity are unacceptably low for current technologies to extract chemicals from lignin. Introducing a selective process to produce value-added chemicals from lignin would guarantee the viability of bio-refineries. Thermo-catalytic conversion of lignin to

valuable chemicals is a promising alternative to add value to the product portfolio of bio-refineries [4].

Development of these catalytic process requires a better understanding of the reaction mechanism and kinetics [1]. Whereas pyrolysis has been studied extensively [5–9], oxidative processes have received less attention. Several studies have examined gasification of lignocellulose—cellulose, hemicellulose, and lignin [6,10,11].

Pyrolyzing lignin produces noncondensable gases, liquids and char [7]. Thermochemical processes break and rearrange the lignin C-H bonds [12]. Reaction temperature, heating rate, gas composition and type of lignin affect the product profile [8]. Gas versus liquid production increases at higher H/C ratio. Low heating rates yield oxygen-containing compounds while high heating rates tend to produce hydrocarbons and alkyl-phenol derivatives [8]. The product distribution depends on the biomass composition [13] but the reaction rate and activation energy are somewhat independent of the composition. The lignin structure, moisture content, impurities, heating rate, and reaction temperature affect the product yield as well as selectivity and the oxygen functional group react over a wide temperature range [8]. Stable low molecular weight compounds form when lignin depolymerizes [4,8].

* Corresponding author.

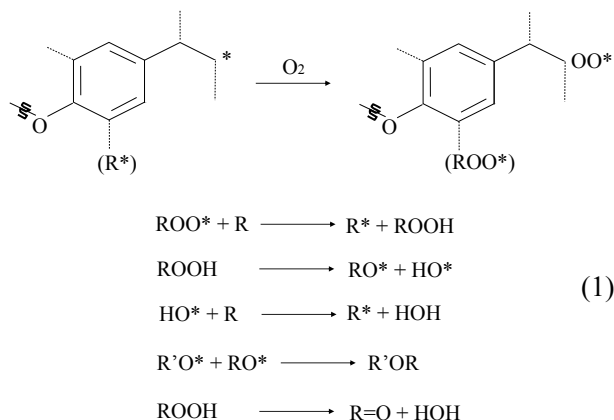
E-mail address: samira.lotfi@gmail.com (S. Lotfi).

Shen et al. [1] proposed a two step kinetic model for wood oxidation in the range of 450 K–800 K. In the first step, lignin decomposed to gas and char and in the second step the remaining fraction produced gas (CO_x) and ash. Wet oxidation hydrolyses lignin to aromatic aldehyde and acids through a consecutive reaction and simultaneously to CO , CO_2 and water. The activation energy of lignin and aromatic aldehyde production were 44 kJ mol^{-1} and 65 kJ mol^{-1} , respectively [14]. Chen et al. [15] derived kinetic model parameters for the decomposition of lignocellulose under a CO_2 environment. A two step mechanism best fit lignin decomposition, where the surface reaction rate was limiting, with an activation energy of 150 kJ mol^{-1} . Blasi et al. reported 86 kJ mol^{-1} for the rapid decomposition of lignin in air [16] that demonstrates lignin decomposition is accelerated in the presence of air.

Oxygen converts most of the lignin to gas and liquids, while after pyrolysis a large fraction remains as char. Pyrolysis of lignin gives coke, gases and liquids including phenolics, non-phenolic, aromatics, and aliphatic compounds [7,8]. Ledesma et al. [17] cracked the 4-vinylguaiacol (2-methoxy-4-vinylphenol) lignin model compound and produced oxygenates (phenols, cresols, furans, ketones, and aldehydes) and aromatic hydrocarbons (single-ring aromatics, and poly-aromatics). The product selectivity changes with temperature and time [18]. Klein et al. [19] reported 10%–20% gas production during lignin pyrolysis. The phenolic fraction typically constitutes 3%–30% of liquid. Beis et al. [19] reached 16–22% liquid yield. The aromatic fraction depends on the type of lignin [19].

Oxygen is a scavenger radical that competes with other rearrangement and radicals compiling reactions. Auto oxidation leads to a series of highly reactive oxygen-based radical, which in further oxidize the lignin structure. In the presence of air, auto-oxidation introduces carbonyl and carboxyl groups to the lignin structure. Oxygen content of lignin increases at temperature less than $\sim 520 \text{ K}$. Beyond 520 K, oxygen content decreases; dehydration reactions, condensation, cross-linking and elimination reactions take place. Keto, ester and anhydride linkages form and water, carbon monoxide and carbon dioxide release (Scheme 1) [20].

Identifying the reaction mechanism could help maintain the catalyst activity and develop strategies to target specific chemicals. Catalyst composition and morphology, heating rate and temperature are the factors that determine the rate at which volatile compounds evolve and provide desired fragments and prevent compounds recondensation and catalyst agglomeration. Many studies characterize the lignin pyrolysis degradation process and wood oxidation but few have evaluated lignin partial oxidations. Here, we tested softwood kraft lignin in both an inert atmosphere and air in a micro-fluidized bed to gauge the product selectivity. We repeated tests in a TGA to examine the kinetics and derive activation energy. One limitation of the TGA is that it is incapable of distinguishing mass changes due to oxygen enrichment [21] or evaporation [22].



Scheme 1. Lignin oxidation mechanism [20].

2. Experimental

2.1. Thermal and thermo-oxidative degradation

FPIInnovations (Quebec, Canada) provided the softwood kraft lignin that was recovered from the Resolute Forest Products mill in Thunder Bay, Ontario via the LignoForce System with a mass fraction of 66.9% carbon, 5.2% hydrogen, 0.1% nitrogen, 25.4% oxygen, and total solid of 92% [23–25].

In the first series of experiments, we heated 500 mg lignin in a 8 mm ID quartz micro-fluidized-bed at 5 K min^{-1} in argon (pyrolysis) and oxygen (21%)–argon (79%) (oxidative degradation) mixture to monitor product selectivity versus temperature. In the second series of experiments, we modelled the reaction kinetics of lignin during pyrolysis (in N_2) and Oxidative thermolysis (in air) using multiple temperature ramps (5 K min^{-1} to 30 K min^{-1}) and iso-thermal tests at 870 K. We adjusted our experiments to the facility of our lab. So, first we did a series of experiments in TGA to obtain weight loss; then, we obtain the product selectivity using micro-fluidized bed reactor, MS, GC-MS and HPLC.

To analysis the products of the micro-reactor, the effluent passed through a water quench to trap the liquid. A Varian HPLC (Prostar) with a Metatherm 87H column and 0.02 N phosphoric acid solution as a carrier analyzed the liquid products. To identify unknowns, we extracted samples from the quench with ethyl ether and injected it in a GC-MS (Agilent 5975C VLMSD) with a capillary column (Br-1ms $15 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$). For liquid-liquid extraction, we measured 10 ml of sample from the quench and poured it in a cone separatory funnel. We added 5 ml ethyl-ether to the funnel and shake the mixture well. After the phases separated, we removed ethyl-ether phase and returned the aquatic phase to the funnel. We repeated this process 3–4 times. A Thermostar Pfeiffer Vacuum mass spectrometer (MS) monitored the composition of the gas after the quench online. A Hanna electrical conductivity (EC) meter measured the concentration of the ionizable solutes trapped by the quench to assess the lignin liquefaction rate. When the bed temperature reached $\sim 500 \text{ K}$ both the MS and EC signals increased noticeably. In fact, the oxygen MS signal decreased while CO , CO_2 , CH_4 , and H_2 increased. So, after 500 K, we began to sample the quench every 10min.

A Thermo-Gravimetric Analyser (TA-Q50) measured the mass loss versus temperature with an accuracy better than 0.1%. We loaded 20 mg sample to a platinum crucible and heated up to 350 K at 10 K min^{-1} under $40 \text{ cm}^3 \text{ min}^{-1}$ flow of nitrogen and held the temperature at 350 K for 15 min to evaporate water. Then we heated lignin at constant ramps include 5, 10, 20, 30 K min^{-1} up to 950 K. For the isothermal tests, we ramped the dried sample at 100 K min^{-1} up to 950 K.

3. Results and discussions

3.1. Product distribution

3.1.1. Thermal degradation

During the lignin pyrolysis tests in the micro-fluidized bed reactor we analyzed both the gas and liquid phases frequently while the temperature ramped up at 5 K min^{-1} . Temperature had a remarkable effect on product distribution as the lignin functional groups react over a broad range (463 K–1000 K). Thermal decomposition of lignin begins with the hemolysis of the weakest bonds like $\beta\text{-O-4}$ to produce phenethyl and phenoxy radicals. The bond dissociation energy of carbon-oxygen (C-O) is 272 kJ mol^{-1} and it is 301 kJ mol^{-1} for C-C bonds. Heating of cross-linked macromolecule structure of lignin generates reactive intermediates [20].

The softwood kraft lignin structure began to crack at $\sim 470 \text{ K}$ (Fig. 1) and first produced CO_2 and CH_4 and reached a maximum at 550 K and 600 K, respectively. At $\sim 550 \text{ K}$, CO first appeared and

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