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A theoretical research on pyrolysis reactions mechanism of coumarone-contained lignin model compound

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ABSTRACT

The coumarone-contained linkage is one of the most important linkages in the lignin structure. To understand the pyrolysis reactions mechanism of lignin, the pyrolysis processes of coumarone-contained lignin model compound were theoretically investigated by employing density functional theory method M062X with the 6-31++G(d, p) basis set. Four possible pyrolytic reaction pathways were proposed and the standard kinetic parameters in all reaction pathways were calculated. The calculation results indicate that the energy barrier of the cleavage reaction of O—C_α bond (244.2 kJ/mol) in pyrolytic pathway (2) is obviously lower than that of the cleavage reaction of C_β—C_α bond (405.1 kJ/mol) in pyrolytic pathway (1), and guaiacol and 8-methoxy-coumarone are formed more easily through pyrolytic pathway (4). The reaction pathways (2) and (4) are the major pyrolytic reaction channels, and the major products of coumarone-contained lignin model compound pyrolysis are 4-methyl-2-methoxy-phenol, 3-methoxy-2-hydroxylphenyl-ethanal, guaiacol, 8-methoxy-coumarone, formaldehyde and so on.

1. Introduction

Biomass is significant feedstock for the renewable production of fuels and chemicals. Thermochemical conversion technology is regarded as a key enabling technology for biomass conversion into high value chemicals and fuels [1–3]. Pyrolysis is the initial step in various thermochemical conversion processes for biomass resources, including combustion, gasification and fast pyrolysis for bio-oil production [4–7]. Biomass mainly consists of three components: cellulose, hemicellulose and lignin, of which the content in biomass varies depending on the biomass type. Lignin is the most abundant resource of aromatic compounds in nature and a main by-product of the pulping process, of which the pyrolysis can obtain value-added aromatic compounds [8]. Lignin is a three-dimensional amorphous polymer consisting of methoxylated phenylpropane structures, and the biosynthesis of lignin is thought to involve the polymerization of three primary monomers: *p*-coumaryl, coniferyl, and sinapyl alcohols [2,9]. These structure units derived from coniferyl, sinapyl, and *p*-coumaryl alcohol are interlinked by a variety of linkages. The linkages include *β*-O-4, 5-5, *β*-1, 4-O-5, *β*-*β*, dibenzodioxocin and coumarone-contained linkages, of which the *β*-O-4 linkage is dominant, consisting of more than half of the linkage structures of lignin [10]. Fig. 1 depicts a schematic representation of lignin structure. Modern NMR (nuclear magnetic resonance) experiments do not confirm the presence of noncyclic *α*-O-4 linkage, but it was suggested that the *α*-O-4 linkage is present only as part of the dibenzodioxocin or coumarone-contained structural unit [2]. The coumarone-contained linkages include both *α*-O-4 and *β*-5 linkages.

The complexity and variability of lignin has resulted in the use of some simpler, low molecular weight lignin model compounds in the study of lignin pyrolysis reactions mechanism [11–15]. Because of the development of the computational techniques and quantum chemistry theory, researchers have paid more and more attention to using quantum chemistry theoretical methods to study the pyrolysis reactions mechanism of lignin. Beste et al. [16,17] theoretically studied the pyrolysis of phenethyl phenylether and its methoxy-substituted derivatives, and reported that the initial step in the PPE (pyrolysis of phenethyl phenyl ether) pyrolysis is the homolytic cleavage of the oxygen—carbon bond, and carbon-carbon bond cleavage in PPE could be a competitive initial reaction. Parthasarathi et al. [18] predicted dissociation tendencies of a diverse set of lignin linkages encompassing 65 lignin model compounds using the density functional theoretical approach, and identified the weakest and strongest linkages connecting arene rings in different classes of lignin model compounds. Liu et al. [19] investigated the pyrolysis of phenethyl phenyl ether (PPE, β-O-4 linkage dimer) as dimeric lignin model compound by

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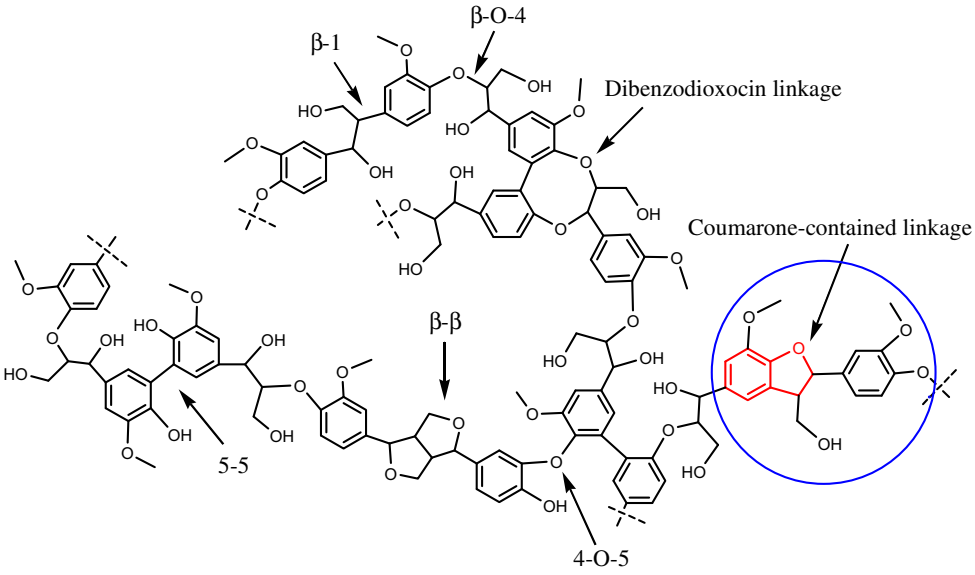
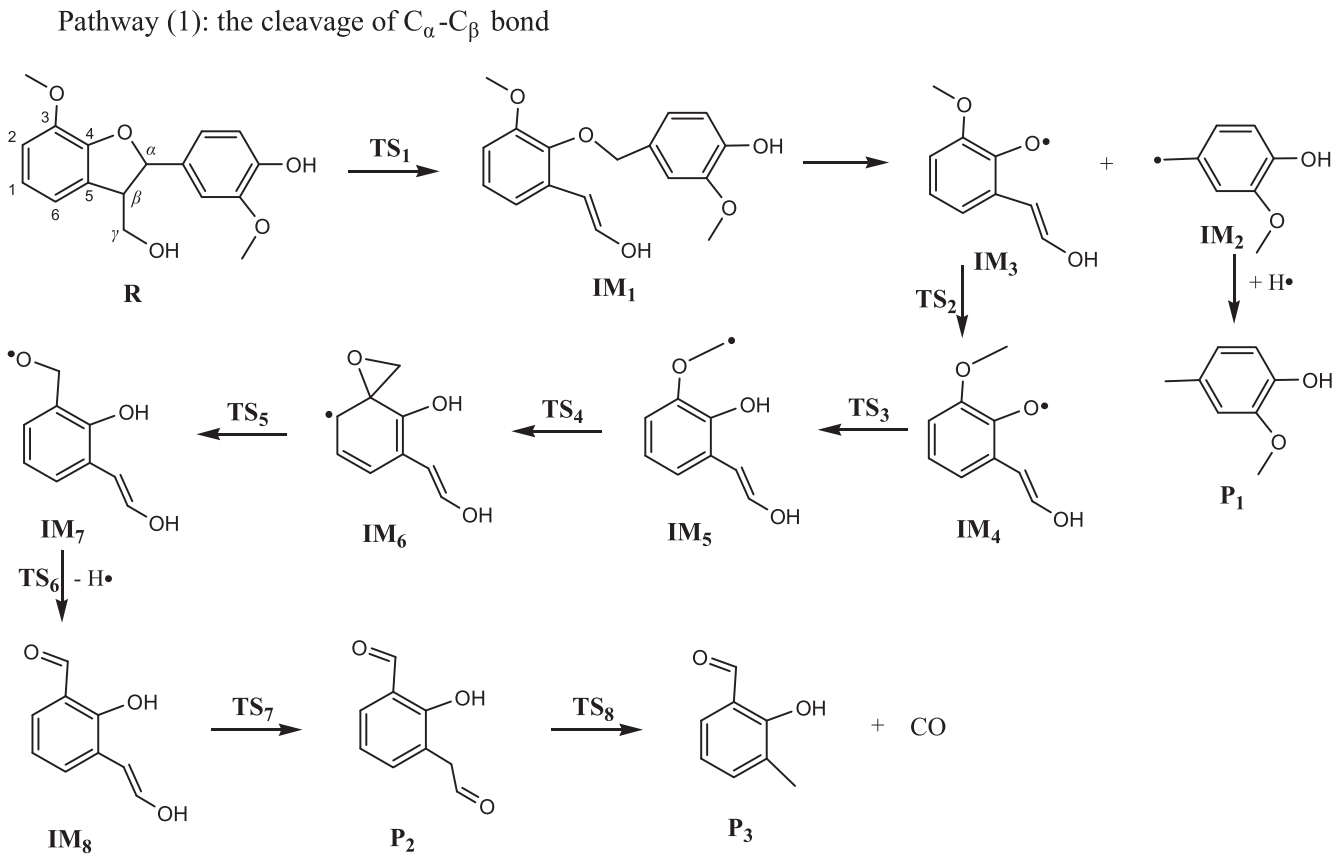


Fig. 1. Schematic representation of lignin structure.

density functional theory methods, and inferred that the major pyrolysis products are styrene, phenol and the compounds that can be formed by combination of benzyl, phenyl, phenoxy and hydrogen radicals. In our previous studies [20–23], we have investigated the pyrolysis reactions mechanism of β-O-4, α-O-4, β-1 linkages lignin dimers. However, there are few report on the pyrolysis mechanism of coumarone-contained lignin model compound. Therefore, in the present study, the pyrolysis processes of coumarone-contained lignin model compound are investigated by using density functional theory methods M062X with the 6-31++G(d,p) basis set in order to understand deeply the lignin pyrolysis mechanism.

2. Calculation methods

All calculations were completed using Gaussian 09 suite of programs [24]. The equilibrium geometries of reactants, intermediates, transition states and products were optimized by using



Scheme 1. Proposed pyrolysis reactions of coumarone-contained lignin model compound in pathway (1).