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Review of NMR Characterization of Pyrolysis Oils

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ABSTRACT: Pyrolysis of renewable biomass has been developed as a method to produce green fuels and chemicals in response to energy security concerns as well as to alleviate environmental issues incurred with fossil fuel usage. However, pyrolysis oils still have limited commercial application, mainly because unprocessed oils cannot be readily blended with current petroleum-based transportation fuels. To better understand these challenges, researchers have applied diverse characterization techniques in the development of bio-oil studies. In particular, nuclear magnetic resonance (NMR) is a key spectroscopic characterization method through analysis of bio-oil components. This review highlights the NMR strategies for pyrolysis oil characterization and critically discusses the applications of ^{1}H, ^{13}C, ^{31}P, ^{19}F, and two-dimensional (2-D NMR) analyses such as heteronuclear single quantum correlation (HSQC) in representative pyrolysis oil studies.

1. INTRODUCTION

Developing viable green energy technologies is imperative because of environmental issues related to fossil fuel usage.[1−3] Utilization of biomass has been introduced as a solution toward the development of sustainable and green energy platforms.[4] Lignocellulosic biomass is a complex composite primarily comprising three principle components: cellulose (~35−50%), hemicellulose (~20−35%), and lignin (~10−25%).[5] Besides these three main components, biomass also has minor components including ash, protein, and other extractives, whose concentrations widely vary depending on the feedstocks. Lignocellulosic biomass is an attractive feedstock for biofuels because it is relatively inexpensive and abundant, avoids the "food or fuel" argument, and is a renewable source of carbon. Typical bioresources for biofuels include energy crops, such as switchgrass, miscanthus, poplar, and energy cane, or biomass residues from agriculture and forestry operations.[6] The U.S. Department of Energy and U.S. Department of Agriculture established a national goal that lignocellulosic biomass will supply 5% of the nation's power by 2020 and 20% of its transportation fuels and 25% of its chemicals by 2030. This goal is approximately equivalent to 30% of the petroleum consumption in the year 2005.[7]

Biomass pyrolysis is a promising thermochemical conversion technology that involves irreversible thermochemical decomposition of lignocellulose in the absence of oxygen.[8] The complex polymer constituents of lignocellulose (i.e., lignin, cellulose, and hemicellulose) are depolymerized into smaller molecules upon thermal treatment. The pyrolysis products contain char, gas, and a pyrolysis oil. In particular, the pyrolysis oil has the potential to be blended in the transportation fuels even though it still has some challenges as a fuel, because of its physiochemical properties (which will be discussed in the following section).[9] In addition, a number of valuable chemicals such as methanol, phenol, catechol, carboxylic acid, and furfural, can be derived from pyrolysis oils.[10] Thus, understanding pyrolysis oil components is an essential part of pyrolysis research, which will provide a fundamental foundation from which future chemical upgrading of bio-oils can be developed.[11]

Various instrumental analytical techniques including gas chromatography (GC), liquid chromatography (LC), high-resolution mass spectrometry (HRMS), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and NMR have been introduced for characterization of bio-oils in the previous studies.[12−16] One of the most comprehensive spectroscopic experiments suited for the comprehensive elucidation of bio-oil components is NMR spectroscopy. Various NMR experiments have been employed to better understand the components and structures of thermally generated bio-oils. ^{1}H and ^{13}C NMR analyses have been widely used to investigate the structural hydrogen−carbon framework of bio-oils.[17] Moreover, selective analysis of functional groups in the pyrolysis oils through NMR analysis techniques allows a deep understanding of the characteristics of pyrolysis oils. For instance, hydroxyl functional groups of bio-oils can be measured by phosphitylation followed by ^{31}P NMR spectroscopy.[18] Likewise, derivatization of bio-oils with 4-(trifluoromethyl)phenylhydrazine followed by ^{19}F NMR spectroscopy provides a quantitative and comprehensive understanding of carbonyl groups, which lead to corrosion and aging problems during upgrading.[19] 2D-NMR experiments, such as $^{1}H-^{13}C$ HSQC, are used to

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