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Model compound approach to design process and select catalysts for in-situ bio-oil upgrading

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A B S T R A C T

Upgrading of pyrolysis bio-oil from biomass suggests great environmental and economical advantages for the production of renewable and sustainable energy sources. However, there are considerable challenges in the development of techno-economically feasible processes and catalysts. One promising approach is in-situ vapor phase upgrading, which demonstrates numerous benefits.

Due to the highly complex nature of bio-oil, understanding the reaction pathways for each kind of compound conversion is highly desirable for catalyst and process screening. Therefore, the study of model compounds is the first step in simplifying the complexity of the problem.

This investigation presents a summary of invaluable model compound based approach research to develop the fundamental processes and catalysts knowledge required to design upgrading strategies of fast pyrolysis bio-oil to achieve a stable product. Key upgrading reactions for the various oxygenated compounds available in pyrolysis vapor, comprising aldol condensation, deoxygenation, alkylation and aromatization are explained. Model compound studies have also been crucial to understanding catalyst behavior for a certain process and identifying potential means to mitigate catalyst deactivation. The knowledge gained from the model compound studies can be correlated to actual pyrolysis bio-oil vapor upgrading.

Contents

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1. Introduction

The importance of renewable energy sources has quickly increased due to the high price of crude oil, high demand of energy resources and environmental concerns caused by the use of fossil fuels. Among various energy resources, biomass recently has attracted significant interest as a promising renewable energy resource [1–4].

The abundance of lignocellulosic biomass and its low price make this feedstock attractive enough. Lignocellulosic biomass can be converted to liquid fuels via the pyrolysis process. Pyrolysis is the thermal decomposition of biomass in the absence of oxygen [2–5].

Fast pyrolysis is one of the most promising technologies for the utilization of renewable biomass resources and it has attracted extensive attention in recent years [5–8]. It is characterized by very high heating rates, moderate temperatures (450–600 °C) and rapid quenching of the pyrolysis products [9].

Bio-oil derived from the degradation of lignin, cellulose and hemicelluloses is a complex mixture of oxygenated compounds. A typical bio-oil can contain more than 400 different compounds [10] with broad molecular range from 18 to 5000 g/mol or more [11]. These oxygenated compounds caused most of the deficiencies of bio-oil, such as its low heating value, adaptation with petroleum fuels, corrosiveness and instability under prolonged storage and transportation conditions [10–13].

For the aim of bio-oil's quality improvement, various approaches have been utilized comprising pyrolysis under reactive atmosphere [14–16], reduced pressure distillation [17], pyrolytic lignin removal [18], pyrolysis vapor upgrading at low pressure [19], high pressure thermal treatment [20], hydro-treatment at high pressure [21], solvent addition [22] and conversion of bio-oil's acidic compounds to esters over acid catalysts [23] and to ketones over base catalysts [24]. Most research efforts however focused on the upgrading of bio-oil by reducing its oxygen content.

While bio-oil was used as a feedstock for in-situ catalytic upgrading, a significant formation of tar and char, which could cause catalyst deactivation and bio-oil yield reduction, was observed during the process [25,26]. These drawbacks can be subsided using an in-situ biomass pyrolysis vapor upgrading process.

The in-situ catalytic upgrading of pyrolysis vapors, over HZSM-5 and HY zeolites in a fixed bed reactor, was carried out by Park et al. [27]. They compared their experimental results with the data from the study of Vitolo et al. [28]. In the case of in-situ catalytic upgrading of biomass pyrolytic vapors, approx. 10 wt% more bio-oil was yielded compared with the use of bio-oil as a feedstock.

As discussed above, one of the most promising processes to achieve upgraded bio-oil is the in-situ catalytic upgrading of biomass pyrolysis vapors. Unlike biomass catalytic pyrolysis, in which catalyst and feedstock are mostly mixed together, in-situ vapor upgrading is performed while biomass and catalyst are separated during the pyrolysis/upgrading process [14]. Pyrolysis vapor upgrading is carried out before vapor condenses, at atmospheric pressure, when vapors are passed through catalyst(s) bed(s). Fig. 1 indicates this type of pyrolysis/upgrading process. Depending on the catalysts' characteristics, different products can be selectively produced while enhanced deoxygenation can yield bio-oil with improved physical and chemical properties. Research is being directed towards the design of selective catalysts for either increasing the production of specific high added value chemicals (e.g. phenols) or minimizing the formation of undesirable bio-oil components (e.g. acids, carbonyls).

Bio-oil contains various oxygenated components originated from different biomass components (cellulose, hemicellulose and lignin) [29,30]. From techno-economical and environmental points of view, the challenge for future bio-refineries will not only include the elimination of oxygen from above mentioned compounds, but also the retention of carbon in the product, with minimum hydrogen consumption [31]. Conventional hydrotreating (HDT) process for bio-oil upgrading could fulfill the requirement of oxygen removal even by high hydrogen

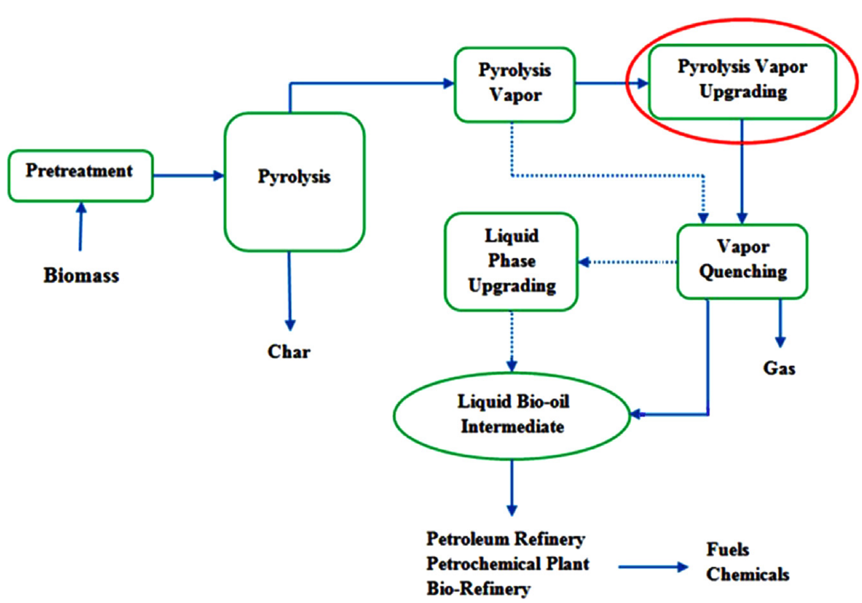

Fig. 1. Schematic of pyrolyis and upgrading process (highlighting pyrolysis vapor upgrading).