



Review

Catalytic fast pyrolysis of biomass over zeolites for high quality bio-oil – A review



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ABSTRACT

Catalytic fast pyrolysis is a prominent technology for yielding high quality bio-oil and chemicals from lignocellulosic biomass while the application of catalyst has been a hotspot for being capable to deoxygenate bio-oil and enhance its fuel properties. The fundamental reaction pathways in catalytic fast pyrolysis and potential routes of bio-oil and chemicals production from three major individual components are discussed at the early section of the review. The effect and potentiality of solid acid catalyst mainly zeolites, biomass particle size and catalyst loading ratio on the yield and quality of bio-oil are then emphasized. In addition, the lumped kinetic model and distributed activation energy model (DAEM), used to predict the thermal behavior of biomass components and energy calculation in catalytic pyrolysis are described. The recent advances in the understanding of catalytic co-pyrolysis of lignocellulosic biomass with hydrogen rich co-feeder from different sources are also presented. The progress with technical difficulties in catalytic pyrolysis is pointed out having an intention to produce high quality bio-oil. Finally, some challenges and perspectives of improving bio-oil quality through catalytic fast pyrolysis that will be significant approach in the future research work are presented.

1. Introduction

The worldwide energy consumption is predicted to thrive due to continuous increase in population and economic growth. According to a rough estimation of daily utilization of liquid fuel in 2017, about 97.51 million barrels (15.503 million m³/day) is being consumed per day [1]. Therefore, securing the available fuel reserves and finding out the alternative energy sources are forthcoming challenges to the globe. Moreover, massive demand for petroleum with depletion of fossil fuels, and environmental concern have motivated researchers towards renewable energy. Bio-oil has become a great interest to be an alternative and promising renewable energy source (lignocellulosic biomass or triacylglyceride) as opposed to fossil fuel because of resource universality and environmental protection [2].

Bio-oil or pyrolysis oil is a dark brown and free-flowing organic liquid having different chemical compositions, such as acids, alcohols, aldehydes, esters, ketones, phenols and lignin-derived oligomers compared with petroleum fuels [2–5]. In spite of being a promising alternative energy source, bio-oil faces several technical difficulties for commercialization due to high acidity (pH 2–3), high viscosity, high moisture, low heating value, corrosiveness and chemically insatiability

[6]. Unlike fossil fuels which poses higher heating value of 40 to 45 MJ/kg, the high amount of oxygenated compounds in bio-oil resulting to its lower heating value of (16.79–19 MJ/kg) coupled with its higher moisture content has been considered as major constraint for the direct use as transportation fuel [7]. According to Imran et al. [8], high acidity, corrosiveness, repolymerization and extreme instability of bio-oil are promoted during storage due to the higher oxygenated compounds and moisture content. Therefore, it is necessary to improve the quality of bio-oil in order to meet the stringent specifications recommended for transportation fuel.

Catalytic fast pyrolysis using a wide range of catalysts has been studied to produce the high quality bio-oil while zeolites with varying pore size and Si/Al ratio favor selectivity of aromatics hydrocarbon [9–11]. Zeolites with different pore size and active site, mostly acidic enhance the deoxygenation reactions of oxygenates and increase the aromatic yield. With the increasing catalytic activity of zeolites modified with Pb, Ni, Zn, Fe, Mo, Ga and Co [12–14], product selectivity has been obtained while catalyst deactivation is one of the main constraints to produce high quality bio-oil. HZSM-5 modified with Ni, Mo, and Ga shows more selectivity compared to Co, Pd-modified catalysts [15] while ZSM-5 modified with Fe possesses better catalytic activity in the

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deoxygenation process hindering the repolymerization of monocyclic aromatic hydrocarbons (MAHs) [16] and exerts more selectivity to BTX (benzene, toluene, and xylenes) through the formation of new active sites [17]. On the contrary, modulated zeolites with the addition of second catalyst phase, like metal oxide phases (ZnO or MgO) exert more selectivity to monocyclic aromatics with a higher energy value as an effect of reduced concentration of Brønsted acid sites in parent catalyst by the generation of additional Lewis acid sites [18–20].

It is necessary to review the recent technological advances in catalytic pyrolysis along with its economic and environmental performance, although several researchers have studied various fast pyrolysis technologies for increasing bio-oil yield. Therefore, the present review concentrates on shape selectivity of zeolites, alteration of number of acid sites and their application to provide the current status of bio-oil production from catalytic fast pyrolysis of lignocellulosic biomass. The review also provides an assessment of biomass particle size along with catalyst to biomass loading ratio for increasing the bio-oil yield and quality. Technical challenges in conducting catalytic pyrolysis in various pyrolysis process have also been elucidated in this review. The final goal of this review is to come up with some recommendations on how to increase the yield of high quality bio-oil from lignocellulosic biomass at a commercial or industrial scale.

2. Catalytic fast pyrolysis for bio-oil

Catalytic fast pyrolysis has received considerable attention in the deoxygenation of pyrolytic vapors and production of aromatics, like BTX (Benzene, Toluene, and Xylene) and phenol [21,22] which has an increasing demand in the petrochemicals industry. Generally, protonation of hydrocarbons starts aromatization at the acidic site of catalysts, which leads to carbonation within hydrocarbons and further reacts to form olefins. On the catalyst's acid site, olefins are then transformed into aromatic hydrocarbons through a series of reactions including oligomerization, cyclization, and hydrogen transfer reaction.

In catalytic fast pyrolysis over zeolites, cellulose produces anhydrosugar at the active site of catalyst through acid catalyzed dehydration [23]. The dehydrated product, anhydro-sugars further transform into C₂-C₆ olefins via oligomerization, decarboxylation and decarbonylation, and finally, olefins combine to yield aromatics demonstrated in Fig. 1. Hemicellulose is more susceptible to thermal degradation due to its noncrystalline nature. Overall reaction pathway of chemicals production in catalytic pyrolysis of hemicellulose is presented in Fig. 2. The major predominant product from pyrolysis of hemicellulose is double-hydrated xylose, which can easily diffuse in zeolite pores and form smaller furanic compounds without any further reactions with low

molecular oxygenating species, like acetic acid, formic acid, acetol, and formaldehyde. Furanic species then undergo a series of catalytic decarbonylation and oligomerization reactions and finally produce aromatics (monocyclic and polycyclic) and olefins through hydrocarbon pool mechanism [24]. In the presence of acid catalyst, like zeolite, sulfated titania and sulfated zirconia, heteopolyacids, MCM-functionalized sulfonic acid, microporous and mesoporous niobium silicates [52,91] xylose undergoes dehydration and produces furfural. It has also noted that furfural transformation generates several hydrocarbons where furfuryl aldehyde, furfuryl alcohol, and 5-hydroxymethyl furfural are prominent [92]. On the other hand, lignin possesses the least susceptibility during catalytic pyrolysis due to complex and three dimensional cross-linked structure of phenyl propane monomers, named guaiacyl, syringyl, and *p*-hydroxyphenyl [25–27]. The potential route for the production of aromatic hydrocarbons from lignin over zeolite catalyst (HZSM-5) is illustrated in Fig. 3 [28]. In catalytic pyrolysis, acid sites of catalysts lead to the scission of C–O and C–C bonds among guaiacyl, syringyl and *p*-hydroxyphenyl produces intermediates, which are comparatively larger to diffuse into zeolite pore and consequently, repolymerizes to coke formation on the zeolite surface which is the main concern in catalytic pyrolysis. Considering this issue, deep understanding of chemical structure and nature of lignin intermediates along with shape selectivity of zeolites are very crucial for decisive reactions in lignin pyrolysis.

Furthermore, several researchers have proposed the aromatic formation through hydrocarbon pool within zeolite catalyst pore in catalytic pyrolysis of biomass [21,29]. An understanding of aromatics formation from a model biomass (cellulose) through hydrocarbon pool is shown in Fig. 4. The first step of catalytic pyrolysis is the formation of anhydrosugars, which results from high heating and homogeneous thermal decomposition of cellulose. The primary pyrolysis products, anhydrosugars are relatively thermally stable and do not favor large amount coke formation in the gas phase [30]. Anhydrosugars undergo further dehydration, bond cleavage, and rearrangement in the gas phase or in the presence of a catalyst to form furanic species, like furan, methylfuran, furfural, 4-methyl furfural and furan-2-methanol, small aldehydes and water [9]. These furan compounds then diffuse into the zeolite catalyst framework and undergo a series of oligomerization, decarboxylation, decarbonylation and dehydration reaction to form hydrocarbon pool and carbon monoxide [9]. The diffusion and hydrocarbon pool formation take almost 2 min, which is much quicker than the thermal decomposition of cellulose. Isotopic study of Carlson et al. [29] revealed that monocyclic aromatics and olefin are produced from hydrocarbon pool. Monocyclic aromatics can further react with oxygenates, like furan to form polycyclic aromatics, such as naphthalene

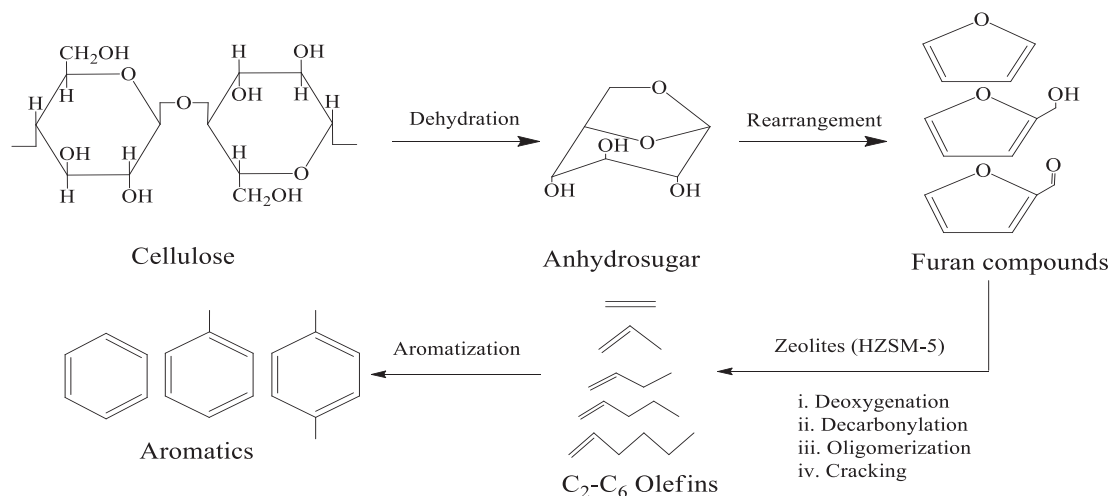


Fig. 1. Reaction chemistry of aromatics production from cellulose over zeolites [23].

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