

Review

In situ fast pyrolysis of biomass with zeolite catalysts for bioaromatics/gasoline production: A review

Ahmad Galadima^a, Oki Muraza^{a,b,*}^a Center of Research Excellence in Nanotechnology, University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia^b Chemical Engineering Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

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ABSTRACT

The fast pyrolysis of biomass-based feedstocks is currently gaining considerable attention as an industrial and sustainable option for the production of gasoline-range bioaromatics. The complex composition of biomass molecules and a series of reactions involved during the upgrading process require the incorporation of sufficiently acidic and topological catalysts. This paper carefully documents and analyzes recent publications that have investigated the properties of zeolites to enhance the yield of bioaromatics during in situ fast pyrolysis. Issues related to the effects of zeolite's textural, topological and acidic properties are critically examined. Factors responsible for catalyst deactivation and the mechanistic roles of the catalysts used are discussed. This paper also explores the prospects of hierarchical zeolites and municipal solid waste (MSW) as catalysts and feedstocks for the fast pyrolysis process.

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1. Introduction

Although fossil fuels will continue to be a critical source of fuel and material for the petrochemical industry in the medium term, their non-renewable nature and environmental inconsistencies have prompted a search for better alternatives. There are a number

of challenging factors that work against the sustainability of these fuels, which are typically associated with serious environmental pollution. The emissions of greenhouse gases such as CO₂ and CH₄ cause global warming due to an associated rise in global temperature with consequential rises in sea levels, flooding and other associated hazards [1–5]. Other emitted gases such as SO₂ promote acid rain, which is destructive and reduces crop yields [6–10]. The destruction of the ozone layer due to fuel combustion permits the transmission of harmful ultra-violet radiation to the Earth's surface; these rays have been identified as causative agents for skin

* Corresponding author at: Center of Research Excellence in Nanotechnology and Chemical Engineering Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia. Tel.: +966 13 860 7612.

E-mail address: omuraza@kfupm.edu.sa (O. Muraza).

and pigment cell cancers [11–13]. Oil spillage during transportation destroys marine environments due to the toxicity of oil to aquatic plant and animal species [14–18]. The limited abundance and non-renewable nature of fossil fuels indicates that they may be depleted in the near future and are therefore associated with significant uncertainties. The global price instability of these fuels has also created economic setbacks to some oil-dependent nations in the recent years with challenges expected to continue in the years to come [19–21]. Among the alternative sources of fuel and material for the petrochemical industry, biomass has significant potential to become more widely used in the near future due to numerous its advantages [22–24]. Significantly reducing humanity's dependence on fossil fuels as energy sources for industrial, residential and agricultural applications is a critical issue. Biomass is typically characterized by complex compositions due to the heterogeneous mixture of organic matter, such as cellulose, hemicellulose and lignin, and inorganic matter, such as carbonates, nitrates, moisture and fluid materials. Biomass resources are widely distributed and abundant globally and are renewable in nature. For example, woody biomass is abundant and distributed in many global regions and countries (Fig. 1) [25]. Biomass-to-fuel conversion processes serve as important methods for the valorization of agricultural derivatives that were once thought of as waste. Other advantages of biomass-based fuels and petrochemical production include decreases in the money invested in foreign oil, reduced emissions of gases (e.g., CO_2 , SO_2 , NO_x) and contributions to global economic sustainability [22,26–28].

As shown in Fig. 2, biomass can be upgraded by many industrial- and laboratory-processes, including transesterification (i.e., for biodiesel production) [29,30]; anaerobic digestion for biogas generation [31,32]; hydrolysis for bioethanol synthesis; hydrotreating for gasoline; diesel and jet fuel based hydrocarbons production; gasification for syngas production and subsequent upgrading to fuels and petrochemicals [33–35], and pyrolysis

[36]. The pyrolysis process entails thermochemical decomposition of biomass-based feedstock at increased reaction temperatures (e.g., 350–700 °C) without the incorporation of air or pure oxygen into the feed. The process yields typically produces irreversible changes in the chemical and physical compositions of the feedstock, creating a net production of gases, liquids and residues. Unlike combustion or hydrolysis processes that involve the incorporation of air, water or a co-reagent as a co-reactant, the pyrolysis process with biomass uses a high temperature as the primary activating agent. Pyrolysis can be slow requiring hours before completion; other the faster methods can complete in seconds or minutes [36]. The fast pyrolysis method, which is the primary subject of this study, has received significant commercial consideration recently because can produce >60% bio-oil with a significant content of valuable gaseous and residual products [37]. For these reasons, the fast pyrolysis process is viewed as an important option by which hydrocarbon compounds in the range for gasoline/diesel could be produced. Recently, Shemfe and co-workers [38] studied a method for upgrading pinewood into fuels. Bio-oil, biogas and char were produced at the rates of 0.64, 0.22 and 0.14 kg/s, respectively. A hydro-treating process was successfully used to upgrade the bio-oil composition into gasoline and diesel range hydrocarbons. Similarly, other pyrolysis by-products can be used as combustion feedstock to fuel the pyrolysis process itself. Microeconomic analysis shows that the pyrolysis process as very profitable. Additionally, several studies have reported a range of fast pyrolysis reaction products with potential to upgrade to valuable fuels and petrochemicals via catalytic routes [36].

Although some reviews have been published on the fast pyrolysis of biomass (see Section 4.1), none have presented comprehensive experimental data derived from recent reactions with zeolites as specific catalysts to enhance the yields of bioaromatics. These studies have emphasized on bio-oil yields and quality and the reaction chemistry involving lignocellulose biomass as a feedstock and catalysts such as oxides, heteropoly acids and supported transition metals. No clear details have been reported regarding the factors responsible for zeolite catalysts deactivation during the process. These missing details will provide researchers with appropriate directions for designing highly active and stable zeolite catalysts that are primarily selective to gasoline-like bioaromatics or paraffins, which is the major challenge associated with the fast pyrolysis process. Zeolite catalysts are given preference for this reaction over oxides, heteropoly acids and supported transition metals for many reasons. The latter catalysts have poor resistance to catalyst poisons that are generated during the reaction; they are also subject to rapid deactivation by coking and can be highly selective to the production of gaseous products instead of the desired liquid hydrocarbons. Conversely, zeolite catalysts are typically characterized by unique structure-acidity properties that improve both their lifetime and selectivity for gasoline-like hydrocarbons. They can also be easily modified with metals or oxides to improve their catalytic performance.

The fast pyrolysis process is commonly classified as an ex-situ and in-situ methods. In the ex-situ method, the catalyst system is incorporated into a separate reactor that is different from the pyrolyzer. Therefore, the catalyst can only make contact with pyrolysis vapor from the pyrolyzer to be upgraded into the desired hydrocarbons. Similarly, the bio-oil from the pyrolyzer can be separated from char and residues for upgrade into bioaromatics in another reactor set-up, containing an appropriate catalyst system. Conversely, the in-situ fast pyrolysis method uses a catalyst and biomass feedstock within the same reactor. Therefore, the catalyst material is intimately mixed with the feedstock, thereby improving the pyrolysis and cracking processes due to the associated improvement in decomposition of large fragments and reduction in char production. Similarly, the catalyst catalyzes the series of

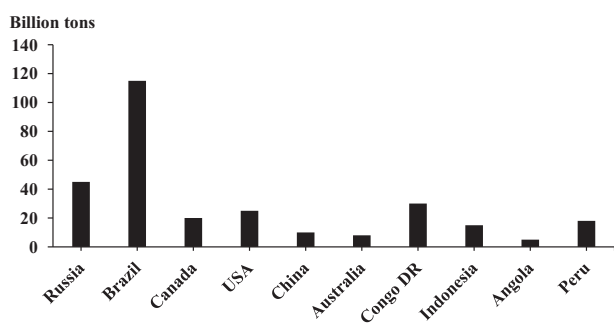


Fig. 1. Woody biomass distribution of key global areas, in billions of tons. Data Source: [25].

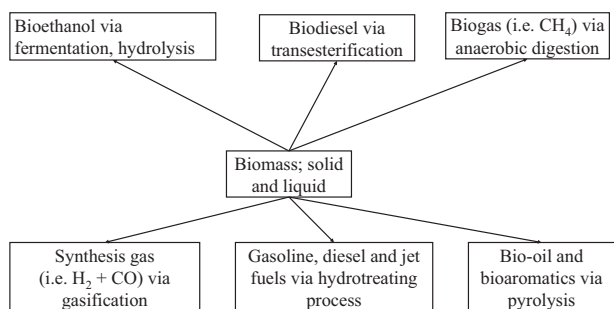


Fig. 2. Some common routes for biomass upgrading.

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