



# Production of green aromatics and olefins by catalytic cracking of oxygenate compounds derived from biomass pyrolysis: A review



Pouya Sirous Rezaei, Hoda Shafaghat, Wan Mohd Ashri Wan Daud\*

Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

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## ABSTRACT

The concern for depletion of fossil fuels and their growing environmental threats necessitates to develop efficient techniques for utilization of biomass as an alternative fuel source which is renewable and environmentally safe. Catalytic cracking of biomass pyrolysis derived feedstock could be an economical process for production of high value added chemicals which are currently obtained from fossil fuels. However, promotion of reaction selectivity toward valuable chemicals is a great challenge in this process. Coke formation in catalytic cracking of biomass pyrolysis vapors/bio-oil is a competing reaction with production of valuable hydrocarbons like aromatics and olefins. Coke is one major undesired product of this process which its high yield is due to low hydrogen to carbon effective ratio of biomass and in turn low hydrogen content in hydrocarbon pool inside catalyst. Catalytic cracking of biomass pyrolysis vapors/bio-oil is a highly shape selective reaction with strong dependency on catalyst acidity and reaction conditions. This paper, for the first time, reviews the effects of catalyst properties and reaction conditions on reaction selectivity toward aromatics and olefins in catalytic cracking of biomass pyrolysis vapors/bio-oil and bio-oil model compounds.

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## 1. Introduction

Current utilization rate of fossil fuels is much higher than their natural regeneration rate leading to the shortage of fossil fuels. Considering the depletion of fossil fuel reserves as

well as the increasing environmental threats like global warming and air pollution caused by large-scale consumption of fossil fuels, there is a growing demand for renewable, sustainable and environmentally friendly fuels [1–5]. Lignocellulosic biomass seems to be a highly potential renewable source of energy. Fuels obtained from biomass are considered carbon dioxide neutral since CO<sub>2</sub> produced from biofuel combustion has been previously absorbed from atmosphere through photosynthesis process of plants [6].

\* Corresponding author. Tel.: +60 3 79675297; fax: +60 3 79675319.  
E-mail addresses: [pouya.sr@gmail.com](mailto:pouya.sr@gmail.com) (P.S. Rezaei), [h.shafaghat@gmail.com](mailto:h.shafaghat@gmail.com) (H. Shafaghat), [ashri@um.edu.my](mailto:ashri@um.edu.my) (W.M.A.W. Daud).

The processes for conversion of biomass into biofuels are generally divided into two broad categories: biological (fermentation and anaerobic digestion) and thermochemical (combustion, gasification, hydrothermal liquefaction and pyrolysis) processes [7,8]. Fast pyrolysis is one of the most promising thermochemical conversion techniques for large-scale exploitation of biomass material and production of liquid fuel [9]. Pyrolysis is the thermal decomposition process in which organic compounds are degraded in an oxygen-free environment. The products of pyrolysis are a liquid fraction called bio-oil (about 75 wt% based on biomass) as well as solid residue containing carbon deposits and non-condensable gases [10]. Pyrolysis derived bio-oil is considered a potential liquid fuel due to its remarkable advantages like slight content of sulfur and nitrogen, renewability and availability of large amounts of biomass and CO<sub>2</sub> neutrality [11].

However, composition of pyrolysis derived bio-oils is different from that of petroleum and contains high content of oxygen and water [12,13]. Bio-oil has low heating value compared to conventional fossil oil, poor thermal and chemical stabilities and high viscosity. It is also corrosive and immiscible with conventional fossil fuels. The corrosiveness is due to high amounts of organic acids which cause a pH value of 2–3 [14–20]. There are typically more than 400 different organic compounds (such as ketones, aldehydes, alcohols, esters, ethers, sugars, carboxylic acids, phenols and furans) in bio-oil which are derived from depolymerization of the three major lignocellulosic components: cellulose, hemicellulose and lignin. Table 1 shows a summary of the main components present in the bio-oil derived from pyrolysis of pine sawdust. This multicomponent composition containing unsaturated compounds causes low stability under storage conditions [21–24]. Due to these drawbacks of bio-oil, it needs to be upgraded.

In the previous years, catalytic treatment has been the focus of many researchers to produce a liquid fuel similar to refined petroleum fuel. Currently, there are two main methods studied for upgrading of biomass pyrolysis liquids. One technique called hydrodeoxygenation (HDO) is a catalytic hydrotreating with hydrogen under high pressure (mostly in the pressure range of 30–140 bar) or in the presence of hydrogen donor solvents [26]. Alternatively, upgrading of biomass pyrolysis vapors/bio-oil can be performed through catalytic cracking using solid acid catalysts under atmospheric pressure without hydrogen consumption [27,28]. Multicomponent composition of bio-oil has attracted several researchers to study the transformation of different bio-oil model compounds such as aldehydes, ketones, acids, alcohols, phenols and their mixtures in order to find out the reaction pathway for their conversion and to determine an overall reaction pathway for conversion of biomass pyrolysis vapors/bio-oil. Several catalyst properties like particle size, pore size, acidity and mesoporosity as well as operational parameters such as temperature, gas residence time and ratio of catalyst to reactants have been reported in literature as the factors which significantly affect reaction pathway and products yields and selectivities. Therefore, it is necessary to design selective catalysts and optimize upgrading process in order to maximize the yield of high value added chemicals and minimize the formation of undesired compounds.

Olefins and aromatic compounds are among the main products obtained by catalytic cracking of biomass pyrolysis vapors/bio-oil. These two hydrocarbon groups are the building blocks of petrochemical industry. Considering the wide range of applications of olefins and aromatics, it seems worthwhile to determine the factors which influence their production in bio-oil upgrading. Selectively production of high yields of green aromatics and olefins through catalytic cracking of biomass pyrolysis vapors/bio-oil can be a viable alternative for production of these compounds from fossil fuel. This work is the first attempt to review the researches held in catalytic cracking of biomass pyrolysis vapors/bio-oil and bio-oil

**Table 1**  
Chemical composition of bio-oil derived from pyrolysis of pine sawdust [25].

| Component or group                  | wt%   |
|-------------------------------------|-------|
| Acids and esters                    | 26.17 |
| Acetic acid                         | 15.33 |
| Formic acid                         | 1.77  |
| 2(5H)-furanone                      | 1.12  |
| Diethoxymethylacetate               | 0.98  |
| Methyl acetate                      | 0.78  |
| Propanoic acid                      | 0.55  |
| 4-Oxopentanoic acid                 | 0.55  |
| Hexyl 2-methylpropanoate            | 0.45  |
| Other acids and esters              | 4.64  |
| Ketones                             | 27.03 |
| 1-hydroxy-2-propanone               | 14.97 |
| Acetone                             | 5.29  |
| 2-Hydroxy-2-cyclopenten-1-one       | 1.89  |
| 3-Methyl-1,2-cyclopentenodione      | 1.06  |
| 1-Acetyloxy-2-propanone             | 0.52  |
| Other ketones                       | 3.3   |
| Aldehydes                           | 19.33 |
| Hydroxyacetaldehyde                 | 10.58 |
| Butanedial                          | 2.15  |
| Formaldehyde                        | 2.03  |
| Heptanal                            | 1.26  |
| Pentanal                            | 1.14  |
| Furfural                            | 0.95  |
| Other aldehydes                     | 1.22  |
| Phenols                             | 8.20  |
| 2-Methoxyphenol                     | 1.18  |
| 1,2-Benzenediol                     | 1.11  |
| 2-Methoxy-4-methylphenol            | 1.07  |
| 3-Methylphenol                      | 1.00  |
| 2-Methylphenol                      | 0.73  |
| Other phenols                       | 3.11  |
| Ethers                              | 0.94  |
| Tetrahydrofuran                     | 0.30  |
| 2-Butyl-3-methyl-oxirane            | 0.16  |
| 3-Methyl-3-(1-ethoxyethoxy)-1-buten | 0.16  |
| Other ethers                        | 0.32  |
| Alcohols                            | 11.45 |
| Methanol                            | 4.59  |
| Ethylenglycol                       | 1.76  |
| Glycidol                            | 0.78  |
| Cyclopropyl carbinol                | 0.73  |
| Other alcohols                      | 3.59  |
| Levogluconan                        | 3.94  |

model compounds with the aim of defining the effects of the catalyst properties and reaction conditions which can change reaction selectivity in favor of aromatics and olefins.

## 2. Catalytic cracking of biomass pyrolysis derived feedstocks

Biomass pyrolysis derived feedstocks can be upgraded using cracking catalysts (zeolites, silica-alumina and molecular sieves) at atmospheric pressure and temperature range of 350–650 °C. Upgrading process can also be integrated with biomass pyrolysis using in situ upgrading technique. In this method which is called catalytic pyrolysis, vapors derived from biomass pyrolysis are directly deoxygenated by passing through a catalyst bed. However, it should be noticed that composition of bio-oil is different from that of biomass pyrolysis vapors due to oligomerization reactions which are occurred through condensation of pyrolysis vapors to bio-oil. This change in composition might cause a difference in product yields obtained from bio-oil upgrading and in situ upgrading of biomass pyrolysis vapors. Being operated at atmospheric pressure without hydrogen consumption, catalytic cracking seems to be economical method compared to HDO [29]. However, some challenges like rapid catalyst deactivation caused by coke deposition, low yields of organic liquids and formation of polycyclic aromatic

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