

# Catalytic Performance Tests for Bio-Oil Upgrading

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## Abstract:

The easiest, and by far the most common, way to carry out a heterogeneously catalyzed gas phase reaction is by passing the gas mixture over a fixed catalyst. Bio-oil is a synthetic fuel under investigation as substitute for petroleum. In the present work, catalytic performance tests for bio-oil upgrading are discussed and reviewed. It is concluded that appropriate catalytic tests in reactors provide insight into bio-oil upgrading mechanism and process scale-up.

## 1 Introduction

Bio-oil, sometimes also known as bio-crude or pyrolysis-oil, is a synthetic fuel under investigation as substitute for petroleum. It is obtained by heating dried biomass without oxygen in a reactor at a temperature of about 500 °C with subsequent cooling. [1, 2] Pyrolytic oil (or bio-oil) is a kind of tar and normally contains levels of oxygen too high to be considered a hydrocarbon. [3, 4] This high oxygen content results in non-volatility, corrosiveness, immiscibility with fossil fuels, thermal instability, and a tendency to polymerize when exposed to air. As such, it is distinctly different from petroleum products. [5, 6] Removing oxygen from biooil or nitrogen from algal biooil is called upgrading. Biofuels are synthesized from intermediary products such as syngas using methods that are identical in processes involving conventional feedstocks, first generation and second generation biofuels. [7, 8] The distinguishing feature is the technology involved in producing the intermediary product, rather than the ultimate off-take. [9]

When wood is heated above 270 °C it begins a process of decomposition called carbonization. If air is absent the final product, since there is no oxygen present to react with the wood, is charcoal. [10, 11] If air, which contains oxygen, is present, the wood will catch fire and burn when it reaches a temperature of about 400-500 °C and the fuel product is wood ash. [12] If wood is heated away from air, first the moisture is driven off and until this is complete, the wood temperature remains at about 100-110 °C. [13, 14, 15] When the wood is dry its temperature rises and at about 270 °C it begins to spontaneously decompose and, at the same time, heat is evolved. This is the well known exothermic reaction which takes place in charcoal burning. At this stage evolution of the by-products of wood carbonization starts. [16, 17] These substances are given off gradually as the temperature rises and at about 450 °C the evolution is complete. [18, 19]

The solid residue, charcoal, is mainly carbon (about 70%) and then of tarry substances which

can be driven off or decomposed completely only by raising the temperature to above about 600 °C to produce Biochar, a high-carbon, fine-grained residue that today is produced through modern pyrolysis processes, which is the direct thermal decomposition of biomass in the absence of oxygen, which prevents combustion, to obtain an array of solid (biochar), liquid-Pyrolysis oil (bio-oil/pyrolysis-oil), and gas (syngas) products. [20, 21] The specific yield from the pyrolysis is dependent on process conditions, such as temperature, and can be optimized to produce either energy or biochar. Temperatures of 400-500 °C produce more char, while temperatures above 700 °C favor the yield of liquid and gas fuel components. Pyrolysis occurs more quickly at the higher temperatures, typically requiring seconds instead of hours. [22, 23, 24] High temperature pyrolysis is also known as gasification, and produces primarily syngas. Typical yields are 60% bio-oil, 20% biochar, and 20% syngas. By comparison, slow pyrolysis can produce substantially more char (50%). Once initialized, both processes produce net energy. [25, 26] For typical inputs, the energy required to run a fast pyrolyzer is approximately 15% of the energy that it outputs. Modern pyrolysis plants can use the syngas created by the pyrolysis process and output 3-9 times the amount of energy required to run. [27]

## 2 Bio-Oil Upgrading

Hydrodeoxygenation (HDO) is a hydrogenolysis process for removing oxygen from oxygen containing compounds. Typical HDO catalysts commonly are sulfided nickel-molybdenum or cobalt-molybdenum on gamma alumina. [28] The first review on HDO was published in 1983. HDO is potentially of interest for producing biofuels, which are derived from oxygen-rich precursors like sugars or lipids. [29] Because of high capital and transportation costs, HDO is not commercially feasible for the deoxygenation of biomass-derived feedstocks. [30, 31] Instead, deoxygenation of biomass typically involve dehydration and decarboxylations.

Pyrolysis is considered the most promising way to convert biomass to fuels. Upgrading biomass pyrolysis oil is essential to produce high quality hydrocarbon fuels. [32] Upgrading technologies have been developed for decades, and this review focuses on the hydrodeoxygenation (HDO). In order to declare the need for upgrading, properties of pyrolysis oil are firstly analyzed, and potential analysis methods including some novel methods are proposed. [33, 34] The high oxygen content of bio-oil leads to its undesirable properties, such as chemical instability and a strong tendency to re-polymerize. Acidity, low heating value, high viscosity and water content are not conducive to making bio-oils useful as fuels. Therefore, fast pyrolysis oils should be refined before producing deoxygenated products. After the analysis of pyrolysis oil, the HDO process is reviewed in detail. [35] The HDO of model compounds including phenolics monomers, dimers, furans, carboxylic acids and carbohydrates is summarized to obtain sufficient information in understanding HDO reaction networks and mechanisms. [36] Meanwhile, investigations of model compounds also make sense for screening and designing HDO catalysts. Then, we review the HDO of actual pyrolysis oil with different methods including two-stage treatment, co-feeding sol-

vents and in-situ hydrogenation. The relative merits of each method are also expounded. [37] Finally, HDO catalysts are reviewed in order of time. After the summarization of petroleum derived sulfured catalysts and noble metal catalysts, transitional metal carbide, nitride and phosphide materials are summarized as the new trend for their low cost and high stability. [38, 39, 40] After major progress is reviewed, main problems are summarized and possible solutions are raised. [41]

### **3 Catalytic Reactor**

Heterogenous catalytic reactors put emphasis on catalyst effectiveness factors and the heat and mass transfer implications. Heterogenous catalytic reactors are among the most commonly utilized chemical reactors in the chemical engineering industry.

A fixed bed reactor is a cylindrical tube filled with catalyst pellets with reactants flowing through the bed and being converted into products. The catalyst may have multiple configuration including: one large bed, several horizontal beds, several parallel packed tubes, multiple beds in their own shells. The various configurations may be adapted depending on the need to maintain temperature control within the system. The pellets may be spherical, cylindrical, or randomly shaped pellets. They range from 0.25 cm to 1.0 cm in diameter. [13] The flow of a fixed bed reactor is typically downward. [42]

A trickle bed reactor is a fixed bed where liquid flows without filling the spaces between particles. Like with the fixed bed reactors, the liquid typically flows downward. At the same time, gas is flowing upward. The primary use for trickle bed reactors is hydrosulfurization. This reactor is often utilized in order to handle feeds with extremely high boiling points.

A moving bed reactor has a fluid phase that passes up through a packed bed. Solid is fed into the top of the reactor and moves down. It is removed at the bottom. [43] Moving bed reactors require special control valves to maintain close control of the solids. For this reason, moving bed reactors are less frequently used than the above two reactors. [44]

A rotating bed reactor holds a packed bed fixed within a basket with a central hole. When the basket is spinning immersed in a fluid phase, the inertia forces created by the spinning motion forces the fluid outwards, thereby creating a circulating flow through the rotating packed bed. [45] The rotating bed reactor is a rather new invention that shows high rates of mass transfer and good fluid mixing. [4] It has mostly been applied in biocatalysis reactions.

### **4 Catalytic Kinetics**

Chemical kinetics, also known as reaction kinetics, is the study of rates of chemical processes. [46] Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism

and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction. The experimental determination of reaction rates involves measuring how the concentrations of reactants or products change over time. For example, the concentration of a reactant can be measured by spectrophotometry at a wavelength where no other reactant or product in the system absorbs light. [47] For reactions which take at least several minutes, it is possible to start the observations after the reactants have been mixed at the temperature of interest.

The mathematical models that describe chemical reaction kinetics provide chemists and chemical engineers with tools to better understand and describe chemical processes such as food decomposition, microorganism growth, stratospheric ozone decomposition, and the complex chemistry of biological systems. These models can also be used in the design or modification of chemical reactors to optimize product yield, [48, 49] more efficiently separate products, and eliminate environmentally harmful by-products. When performing catalytic cracking of heavy hydrocarbons into gasoline and light gas for example, kinetic models can be used to find the temperature and pressure at which the highest yield of heavy hydrocarbons into gasoline will occur. Chemical Kinetics is frequently validated and explored through modeling in specialized packages as a function of ordinary differential equation-solving (ODE-solving) and curve-fitting.

## 5 Concluding Remarks

In the present work, catalytic performance tests for bio-oil upgrading are discussed and reviewed. Fixed-bed reactors are the most commonly used reactor types for testing bio-oil performance evaluations. It is concluded that appropriate catalytic tests in reactors provide insight into bio-oil upgrading mechanism and process scale-up.

## 6 Acknowledgments

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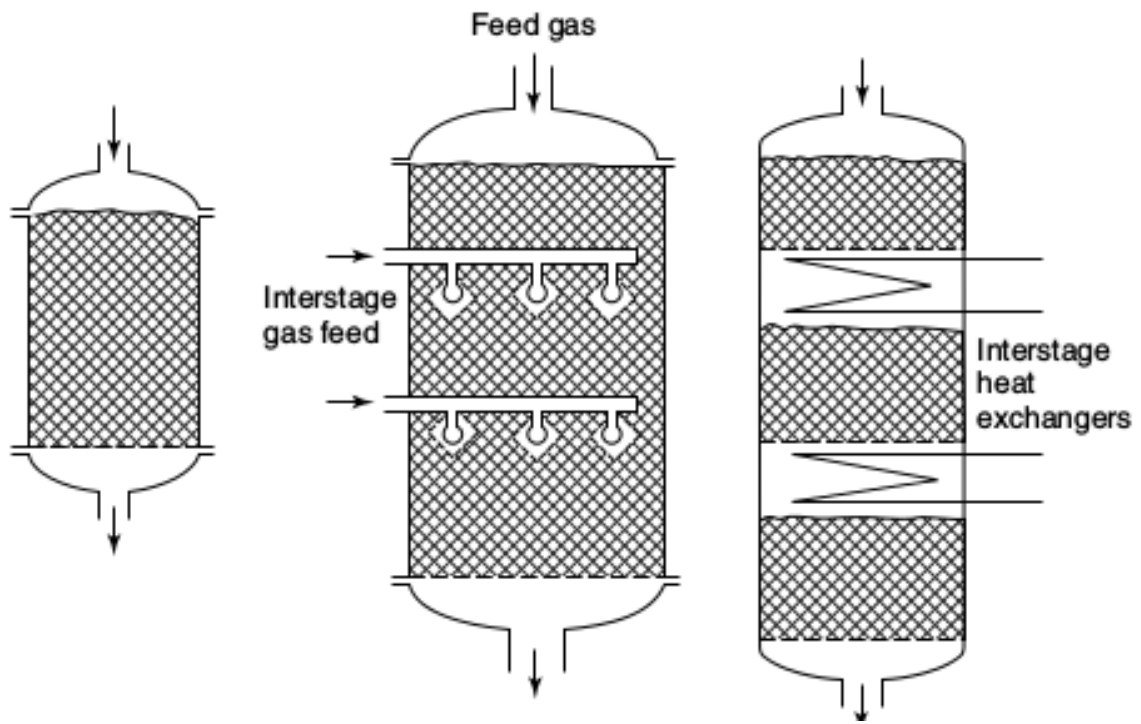


Figure 1: Catalytic Performance Tests for Bio-Oil Upgrading

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Catalog: ***Catalytic Performance***

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