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Research paper

A funnel plot to assess energy yield and oil quality for pyrolysis-based processes

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ABSTRACT

The conversion of biomass to hydrocarbon transportation fuels presents unique challenges that generally focus on maintaining high mass and energy yields while removing oxygen from the biomass. Among the many processes proposed and demonstrated, processes that can achieve this efficiently and economically will have a clear advantage. Currently, there is no graphical method to analyze such conversion processes. In this work, we introduce a Funnel Plot to indicate both product quality, in terms of oxygen removal, and energy yield, the energy retained in the product oil from the original biomass. The Funnel Plot is applied to literature data for several processes and compared to an idealized chemical conversion of biomass revealing some of the current challenges associated with biofuel production.

1. Introduction

Utilizing biomass as a feedstock for renewable transportation fuels and chemicals is becoming increasingly important as worldwide population increases and oil reserves decrease. Over the past ten to fifteen years, research and development efforts have rapidly expanded in efforts to partially displace the world's reliance on fossil fuels. There are a number of different approaches taken to convert biomass to fuels including extracting biomass sugars and transforming them to fuels and chemicals (sugar platform) [1–3], gasification [4], and pyrolysis (thermal platform) [5–9].

Thermochemically converting solid biomass into liquid transportation fuels that are interchangeable with petroleum-derived liquid fuels presents significant technological challenges [10]. Biomass feedstocks are highly variable, non-homogeneous and solid. In addition, the biomass feedstock is oxygen-rich and hydrogen-deficient when compared to crude oil. For example woody biomass is comprised of approximately 50% carbon, 44% oxygen and 6% hydrogen, whereas a typical crude oil is oxygen-free with a hydrogen-to-carbon ratio of 1.76, compared to 1.45 for wood. Considering that gasoline and diesel fuel are oxygen-free with a hydrogen-to-carbon ratio of 1.9–2, the process path from crude oil to fuels is favorable relative to starting with biomass. As a result, the overall path to produce a final finished liquid fuel from biomass will typically require multiple chemical transformations, often catalytic to both remove oxygen and add hydrogen [11,12]. The challenge, then, is to both physically and chemically transform biomass into a hydrocarbon fuel while obtaining favorable economics.

Economics are sensitive to feedstock cost, process yields and in some cases operating costs, in particular if expensive catalysts are used that need frequent replacement [13]. Efforts to remove oxygen can be relatively complex and are typically met with a decrease in both mass and energy yields [14]. Mass yields of the hydrocarbon oil will decrease because of the oxygen removal from the biomass as well as the formation of light gases and permanent char that forms from recalcitrant biomass fractions.

As thermochemical biomass-to-liquid fuels processes are developed and modified, it can be difficult to compare the effects of these modifications on process yields and oil quality in a straightforward manner. Furthermore, it can be very frustrating to compare processes in literature when researchers use different conventions to report process yields, e.g. one reference provides carbon yields, one reference provides mass yield and specific higher heating values (HHVs in MJ/kg), and another reference provides mass yield and atomic composition. This situation is further exacerbated when there is a multi-step conversion or when additional inputs, such as natural gas, are used in the overall process. In this letter, we introduce a Funnel Plot that describes both the product quality and the mass and energy yields of a process. The Funnel Plot allows a straightforward comparison of different thermochemical processes

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for converting biomass into a hydrocarbon fuel.

2. Results and discussion

To introduce the Funnel Plot, results from conventional fast pyrolysis of different feedstocks are compared in Fig. 1 [15–18]. Data are plotted as fractional energy yield, which is the total energy of the product divided by the total energy of the biomass feedstock (HHV basis), vs. mass yield. The dashed lines are lines of constant energy density with slopes equal to the ratio of the specific HHV of product or intermediate to the specific HHV of the biomass feed. There are two lines which form the boundaries of a funnel. The right funnel boundary is a line with a slope of unity defined by the HHV of the biomass feedstock (20 MJ/kg in this case) and the left funnel boundary, with a slope of 45/20, is arbitrarily defined by the upper limit for HHV of petroleum fuels, ≅45 MJ/kg, corresponding to complete oxygen removal from the biomass. Intermediate lines corresponding to HHV values between 20 and 45 MJ/kg are plotted for perspective. Since energy density is less sensitive to hydrogen content than to oxygen content, the dashed lines are useful for plotting data where mass yield and CHN–O composition were provided, but no energy data were provided. Data near the right boundary have similar energy densities and atomic compositions to the feedstock, and data near the left hand boundary have energy density and atomic composition similar to hydrocarbons. The goal of any conversion process is to traverse from right to left while remaining near the top of funnel, i.e. avoid circling the drain due to excessive energy yield losses.

Using a biomass feedstock, i.e. wood, with an energy density (dry basis) of 20 MJ/kg, the starting point on the plot prior to any chemical/physical transformation is at a mass and energy yield of one and located at the top right of the funnel. Energy yields for biomass-to-fuel processes are often presented using specific energy yield, e.g. Gallons of Gasoline Equivalent (GGE = 120.3 MJ) per metric ton (MT) of feed. Therefore, we have included a secondary y-axis that presents yields in GGE per metric ton of feed. This axis is helpful for plotting data, but it also clearly emphasizes the practical limitations for biomass conversion yields to transportation fuels using terms that are familiar to the layperson.

Reactions 1 and 2 in Fig. 1 represent the ideal overall transformations of woody biomass to an alkane (cyclohexane) and an aromatic (benzene) compound assuming that no other source of hydrogen or carbon are added to the process and all oxygen is removed through formation of carbon dioxide and water which results in a theoretical energy yield loss of about 10%. These points for theoretical hexane and benzene are plotted on the upper left side of the funnel.

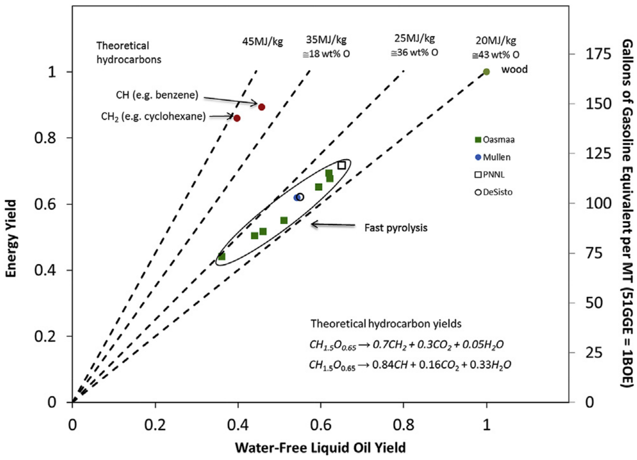

Fig. 1. Funnel Plot of pyrolysis oil generated from the fast pyrolysis of different feedstocks: 🟩Oasmaa [18], ○DeSisto [15], ●Mullen [17] and ☐PNNL [16].

The stoichiometries for producing cyclohexane (CH_2) and benzene (CH) from wood ($CH_{1.5}O_{0.65}$) are presented in Equations (1) and (2).

$$CH_{1.5}O_{0.65} \rightarrow 0.7CH_2 + 0.3CO_2 + 0.05H_2O \quad (1)$$

$$CH_{1.5}O_{0.65} \rightarrow 0.84CH + 0.16CO_2 + 0.33H_2O \quad (2)$$

Equation (1) shows that the optimal saturated hydrocarbon product yield is obtained when approximately 90% of the oxygen is removed as CO_2 during the overall processing. This optimum results in a carbon yield of 70%, and a mass yield of 41% for the biomass composition used in the example. Unfortunately, real processes suffer from additional yield losses. In fact, each stage of transformation, oxygen removal, and upgrading can result in significant energy yield losses as shown by the data for the initial transformation of wood to liquids by conventional fast pyrolysis plotted in Fig. 1.

2.1. *Conventional fast pyrolysis*

Fast pyrolysis consists of rapidly heating biomass (~1–2 s residence times) at intermediate temperatures (~500 °C) in an inert atmosphere. Traditionally, the fast pyrolysis process is optimized for producing a liquid product with maximum mass yield. Other primary products include a solid char phase and permanent gases (CO, CO_2, CH_4, etc.). Although the liquid yield is high, the oil produced is of rather poor quality as a fuel due to acidity, water solubility and high oxygen content. Data points for fast pyrolysis oil produced in this manner were taken from the literature [15–18]. Data are included for a variety of feedstocks including pine sawdust, fresh and stored forest residues, eucalyptus, barley straw, timothy hay, and reed canary grass [18]; pine sawdust [15]; mixed wood [16]; and white oak wood [17]. It is clear that the energy yields vary with the biomass feedstock. Additionally, yields will vary with reactor type. Despite these variations, the mass and energy losses associated with fast pyrolysis are clearly presented in the plot relative to the initial feedstock. The drop down the funnel indicates yield losses in the form of char and permanent gases. The relatively poor quality of the oil is also clear as the points all lie to the far right of the funnel. Therefore, significant further processing would be required to create hydrocarbon liquid fuels. Also note that a process purporting to convert wood to gasoline with a yield greater than 125 GGE/tonne using fast pyrolysis as the primary conversion method would be highly suspect according to the secondary y-axis on the plot.

2.2. *Pyrolysis processes that improve oxygen removal and oil stability*

The chemical characteristics of conventional pyrolysis oil can present challenges for its use as either a fuel or feedstock for further upgrading. This has led to the development of alternative pyrolysis processes with the general goal of further oxygen removal during the pyrolysis step, thereby increasing oil chemical stability, and subsequently decreasing the complexity of upgrading to a drop-in fuel. Additionally, if significant quantities of oxygen are removed, the resulting pyrolysis oil may have additional uses that don't require upgrading. Data obtained from the literature for several alternate processes are shown on the Funnel Plot in Fig. 2, along with data from conventional pyrolysis.

Using a hot gas filter to remove char after initial pyrolysis is an