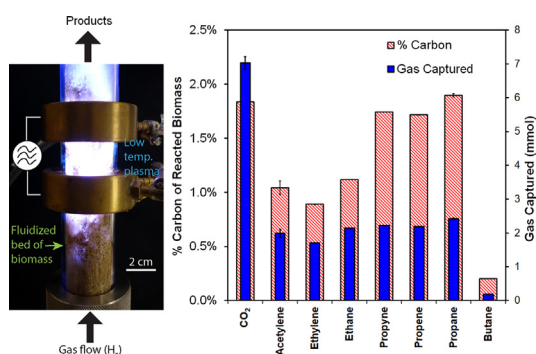Full Length Article

Accessing unconventional biofuels via reactions far from local equilibrium

Yu Gao, Necip B. Uner, Elijah Thimsen*, Marcus B. Foston*

Department of Energy, Environmental & Chemical Engineering, Washington University in St. Louis, 1 Brookings Drive, Saint Louis, MO 63130, USA

GRAPHICAL ABSTRACT

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ABSTRACT

The thermochemical production of fuels from lignocellulosic biomass is constrained by equilibrium thermodynamics. However, low temperature plasma reactions are not governed by local equilibrium and involve the formation of unique radical and ion species. Thus, low temperature plasma can open pathways in the conversion of lignocellulosic biomass to products not observed in conventional thermochemical processing. In this effort, a novel radio-frequency (RF) plasma-enhanced fluidized bed reactor was utilized for the low temperature plasma deconstruction of lignocellulosic biomass in a hydrogen background gas. Of the reacted biomass in the plasma, 35% of the carbon was converted into hydrocarbons. Specifically, 16.9, 8.2, 9.6, and 0.2% of the reacted carbon from the biomass was converted into CH_4, C_2H_x, C_3H_x, and C_4H_x, respectively. With increasing power input, more rapid conversion of biomass was achieved, while the total amount of carbon from the biomass converted into hydrocarbons was similar.

1. Introduction

A significant challenge for large-scale biomass utilization is related to the generation of value-added products, *i.e.*, biomass-derived drop-in fuels, chemicals, and materials. Established thermochemical methods of deconstructing biomass, such as gasification and pyrolysis, have the advantage of rapid kinetics and provide possible routes to precursors for the synthesis of such products. Gasification processes (> 1000 K) result in the decomposition of biomass towards an equilibrium composition comprised mainly of CO and H_2, also known as synthesis gas. The conversion of synthesis gas to higher value hydrocarbon products can then be accomplished *via* Fischer–Tropsch chemistry. However, production of Fischer–Tropsch liquids from biomass has not seen widespread commercial deployment [1]. Thermal pyrolysis (~300–900 K) employs similar biomass decomposition pathways that are selected for by lower reaction temperatures and operate under local equilibrium to generate kinetic products such as bio-oil. This bio-oil product is a heterogeneous mixture of acids, alcohols, aldehydes, esters,

ketones, sugars, phenols, guaiacols, syringols, and furans, which must then undergo several subsequent resource-intensive upgrading processes, such as hydrodeoxygenation, before the products resemble precursors useful in the production of fuels [2].

A major challenge with thermochemical processing of biomass is that known processes generate either a product of little direct value (*e.g.,* synthesis gas *via* gasification) or a heterogeneous mixture with low selectively for any given species (*e.g.,* bio-oil). Developing a biomass conversion method that benefits from the same advantageous kinetics observed for thermochemical processing but affords direct access to more commercially valuable product distributions would be tremendously useful. However, that goal represents a major technical challenge (*vide infra*).

Plasmas are ionized gases that can be classified into two main groups: high and low temperature. High temperature plasmas, or thermal plasmas, are characterized by electrons, ions, and neutrals being in *local thermal equilibrium* at a very high temperature, typically in excess of 3000 K. On the other hand, low temperature plasmas are a non-equilibrium substance wherein *local equilibrium cannot be assumed*. For example, the heavy species in a low temperature plasma, such as neutral gas molecules and ions, are typically $T < 1000\,K$, but the free electrons are very hot, often $T_e > 20,000\,K$. In other words, temperatures of species in a low temperature plasma may be different by an order of magnitude at the same location in space. The very hot electrons cause a plethora of reactive kinetically-controlled processes when collisions occur with neutral gas molecules and surfaces. Examples of such reactive process include: electron impact dissociation or excitation, spontaneous photoemission, ionization, etc. [3]. These highly energetic kinetic processes are expected to deconstruct biomass easily. Also, many of the reactions occurring during deconstruction of biomass are known to involve radical and ionic intermediates [4,5]. Unique radicals and ions may be generated in low temperature plasma that open pathways with rapid kinetics to products that are inaccessible via conventional thermochemical routes governed by local equilibrium. Moreover, from the perspective of thermodynamics, low temperature plasma processes must obey the 1st and 2nd laws; however, the product distributions resulting from plasma processes are not constrained by equilibrium thermodynamics. In fact, low temperature plasmas are capable of moving chemical systems away from equilibrium. For example, it has been observed that when pure CO_2 is fed into a low temperature plasma at conditions where it is the thermodynamically stable species of carbon, it can be split and significant quantities of CO are formed with carbon mole fraction of approximately 70% [6]. Additionally, it is well known that if pure O_2 is fed into low temperature plasma, the effluent may contain a mole fraction of up to 10% O_3, which is again a move away from equilibrium [7]. Due to these alluring features, low temperature plasmas have begun to attract attention for processing biomass. The focus in this paper is on converting the biomass into hydrocarbons, which are useful as polymer precursors (*e.g.,* ethylene) or transportation fuels (*e.g.,* propane and butane).

Vanneste et al. recently published a review on the application of low temperature plasma for pretreatment of lignocellulose [8]. There are published examples of biomass deconstruction by low temperature plasma, but knowledge of product distributions is limited [8–12]. There have been a few published studies that do detail the product distributions generated in high temperature thermal plasmas [13–16]. Typical product distributions from these high temperature systems governed by local equilibrium are similar to thermal gasification of biomass with approximately 65 wt% yields of gas, principally comprised of CO and H_2, and the remainder of carbon in the form of char. Summaries within studies by Shie et al. [11] and Huang et al. [14] concisely review research conducted on plasma-based pyrolysis and gasification technologies, demonstrating the opportunity for more detailed study. Accordingly, for low temperature plasmas in which local equilibrium cannot be assumed, there remains a large number of gaps in knowledge about the biomass processing application.

In this work, a low temperature plasma was used to deconstruct lignocellulosic biomass in a hydrogen background gas. To improve the plasma-biomass contact area, a low temperature plasma-enhanced fluidized bed reactor was utilized. In the plasma reactor, switchgrass was reacted and a significant fraction of the carbon atoms fed into the plasma reacted to form hydrocarbons. The distribution of these hydrocarbons contained a significant fraction of methane, but contained also heavier species such as propane and butane.

2. Materials and methods

2.1. Chemicals

Switchgrass (*Panicum virgatum*; Wiley milled and sieved 80 to 20-mesh fraction; James R. Frederick, Pee Dee Research and Education Center, Clemson University, Florence, SC) was Soxhlet extracted with ethanol:toluene (2:1) and then water overnight. All gases were purchased from Airgas and all reagents were purchased from Sigma-Aldrich.

2.2. Plasma-enhanced fluidized bed reactor (PEFBR)

The reactor employed in this study is unique in the sense that it is capable of homogenously treating 10–100 g scale biomass by direct plasma contact. In a recent review, Vanneste et al. noted that a dynamic high-throughput reactor for uniform plasma treatment of biomass is a major challenge for potential industrial application [8]. The plasma-enhanced fluidized bed reactor (PEFBR) exactly fulfils these needs because of the constant mixing of solids provided by fluidization. Low pressure operation provides a large plasma volume, and ensures good contact between the particles and the plasma. Furthermore, using RF power and the placement of the electrodes outside of the reactor prevents electrode contamination and provides robust operation.

The PEFBR is a batch system comprised of a reaction zone, a liquid nitrogen trap for collection of condensable species, and a quadruple mass spectrometer (QMS) for online measurement of the effluent composition. A schematic of the system is presented in Fig. 1a. The reactor consisted of a vertical fused silica tube of 120 cm height and 3.8 cm outer diameter. A quantity of 22.2 g of dried switchgrass (35–50 mesh size) was loaded in to the reactor. The switchgrass rested on a sintered metal filter that acted as a flow distributer. Switchgrass particles were found to be difficult to fluidize since they are light and prone to channeling. To enhance fluidization and prevent channeling, 30 g of 400–600 μm diameter glass beads, which were assumed to be chemically inert, were added to the reactor. A second sintered metal filter was placed on the outlet of the fused silica tube to prevent elutriation of fine particles into the vacuum system. The system was pumped down, and then a constant flow of 600 standard cubic centimeters per minute (sccm) of grade 5.0 H_2 was flowed upwards, causing the mixture to fluidize. The pressure measured upstream of the bottom sintered metal filter was 3.2 kPa and downstream of the top sintered metal filter was 1.7 kPa. The average of these values was taken as the reaction pressure of 2.5 kPa. Plasma was generated by coupling radio frequency power (13.56 MHz) to two brass ring electrodes around the tube. The electrodes were water cooled and they were placed just above the bed. Unless otherwise stated, the applied power was 275 W. The bed fluidized in a slugging regime and plasma was generated in the large gas bubbles within the bed, forming a reaction zone with an approximate power density of a few W cm^{-3} (see Fig. 1b).

The effluent from the PEFBR was passed through a liquid nitrogen trap to collect condensable species. The liquid nitrogen trap had valves on the inlet and outlet, and thus, it could accommodate positive pressures up to 100 psi, allowing for the condensed products, some of which had boiling points below room temperature, to warm up safely to room temperature after the reaction was complete. The lines between the reaction zone and the liquid nitrogen trap were maintained at room