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Biomass fuel bound nitrogen (FBN) conversion in two fluidized bed gasifiers

Background

When biomass is gasified, its fuel bound nitrogen (FBN) converts into five major forms (N_2 contained in the gasifying agent(s) is not reactive at fluidized bed gasification temperatures) (Figure 1). The ammonia (NH_3) and hydrogen cyanide (HCN) in the syngas are of particular interest because they are NO_X precursors if the syngas is combusted. They are catalyst poisons if the syngas is to be utilized for chemical or syn-fuel products. It is of interest to determine gasifier operating conditions that minimize conversion of FBN to NH_3 and CHN.

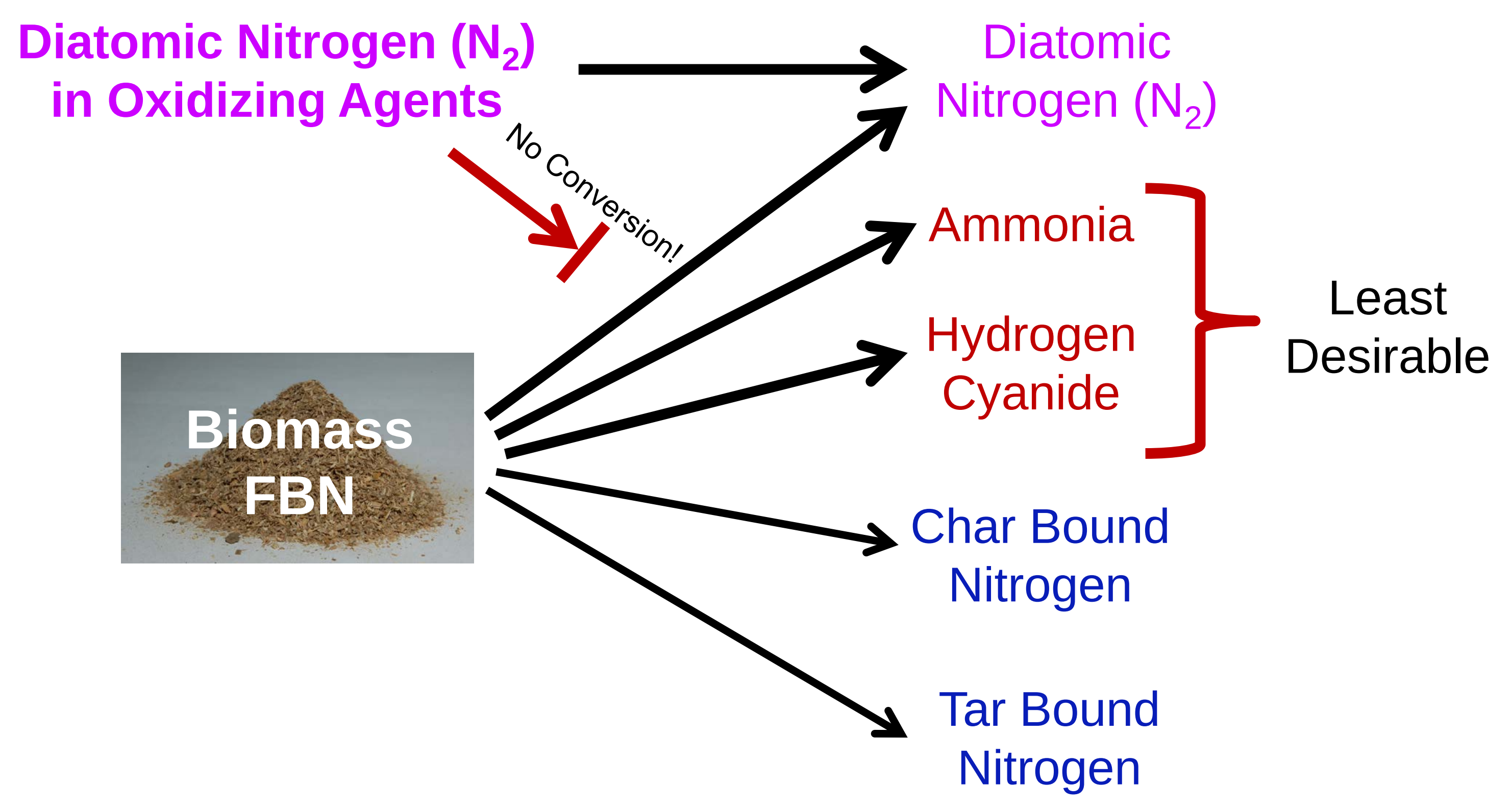

Figure 1. The five major nitrogen bearing products of gasification.

The concentrations of nitrogen in feedstocks can vary by nearly two orders of magnitude [1], leading to NH_3 and HCN concentrations in syngas which also vary widely [2-7]. Equilibrium modeling using software programs such as STANJAN demonstrate that NH_3 and HCN should be minor products of gasification, yet for typical gasification conditions, well over half of the FBN is converted to NH_3 or HCN.

Materials and Methods

Two fluidized bed gasifiers were used in these tests: A pilot-scale 20 kg/h gasifier and a laboratory-scale 0.1 kg/h gasifier. The large gasifier was designed to approximate adiabatic operation and used a steam-oxygen mixture (36% oxygen) as fluidizing agent. The equivalence ratio (ER) was varied to explore its affect on NH_3 and HCN yields. Gas samples were extracted from the large gasifier via an iso-kinetic sampling line (Figure 2). Char was removed via a hot ceramic filter. Tars were removed for gravimetric analysis via a dry condensing method. Liquid samples of nitrogen compounds were collected using glass impingers. 5% HCl was used to collect NH_3. 100 mM NaOH was used to collect HCN.

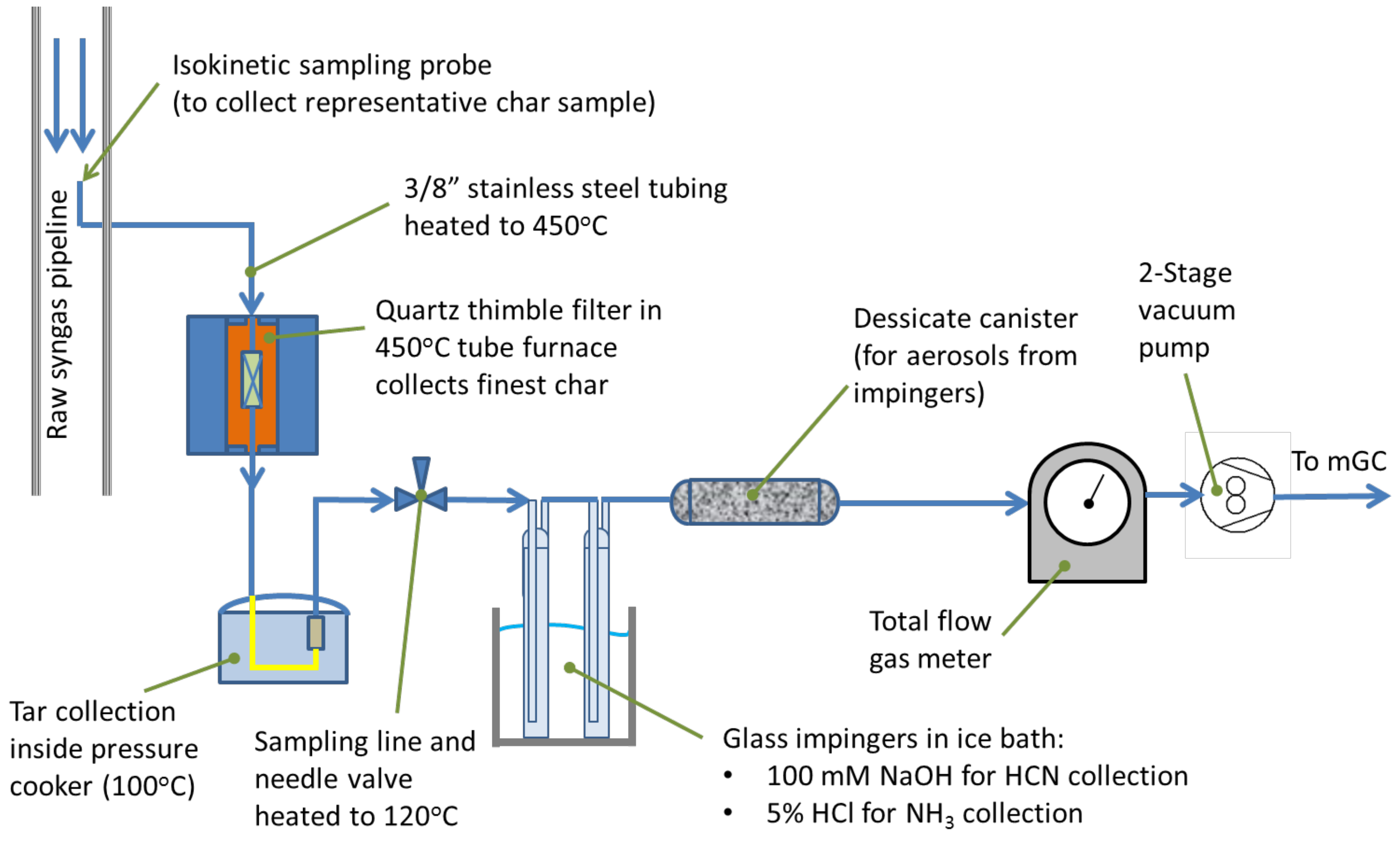

Figure 2. Sample line setup for measurement of char, heavy tar, water, major permanent gas, and nitrogen compound composition of the syngas from the 20 kg/h gasifier. Gas sampling on the small reactor was conducted in a similar manner, but using an electrostatic precipitator instead of a tube furnace and dry condenser.

The small gasifier was operated allothermally (ER of zero). The short residence time of this reactor (1.2 s) allowed us to investigate the primary products of FBN devolatilization. Tars were removed via an electrostatic precipitator instead of a pressure cooker. Due to the reactor's small size, all of the syngas produced by the reactor was bubbled through the impingers, rather than using a slip stream. A drum-type gas meter was used for both small and large scale tests to measure the total flowrate through the sampling lines.

Depending on the anticipated amount of NH_3 and HCN, two to four impingers were used in series. Gas was allowed to flow through the impingers at 1.0 SLPM for 30 min per sampling session (Figure 3). After sample collection, the resulting NH_4^+ solution was analyzed via distillation and titrimetric analysis. The CN^- solution was analyzed via Ion Chromatograph (Figure 4).

Figure 3. Collecting liquid samples of nitrogen compounds using glass impingers downstream of tar condensing pressure cooker.

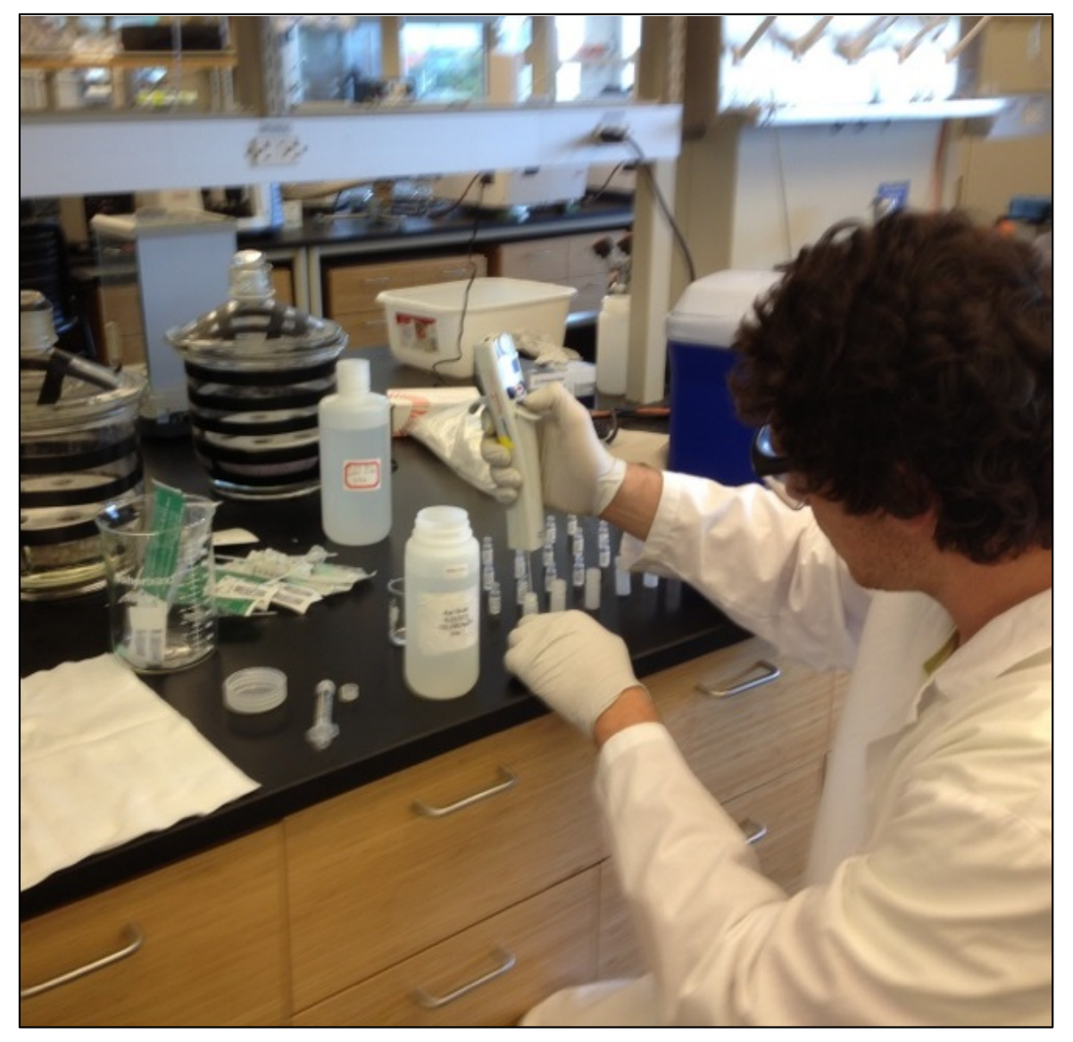

Figure 4. Preparing CN^- samples for Ion Chromatograph analysis.

Results for tests in the 20 kg/h gasifier

Ammonia was higher in concentration than HCN for all tests in the large gasifier; however, HCN was still present at much higher concentrations than presented by other researchers [2-7] (Figure 5).

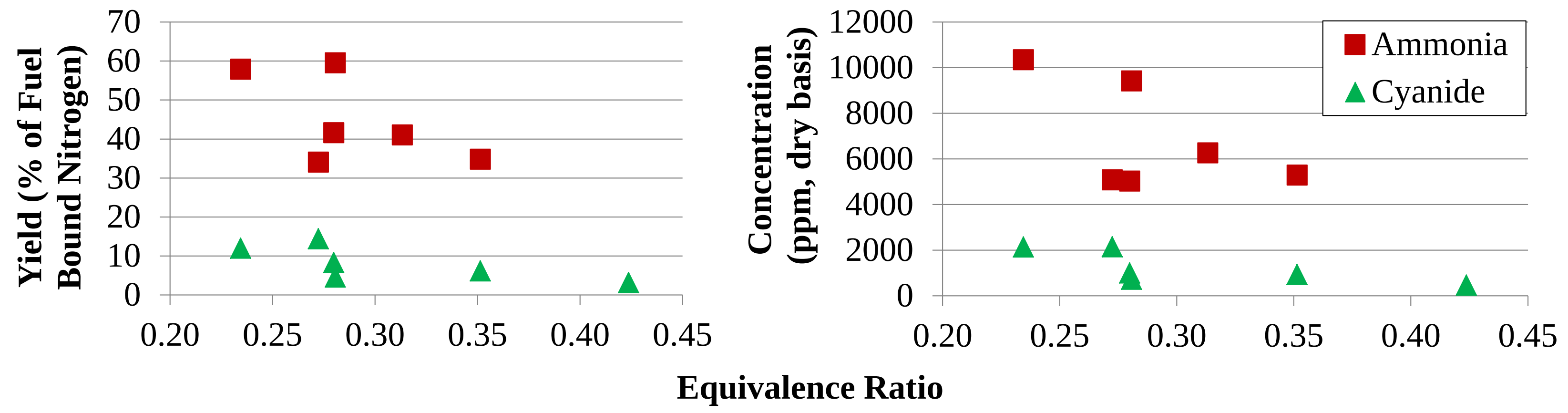

Figure 5. Percent yield and concentration data for NH_3 and HCN in syngas produced by the 20 kg/h gasifier in response to changes in equivalence ratio.

Results for tests in the 0.1 kg/h gasifier

Allothermal gasification in the small gasifier revealed that it is possible for HCN concentrations to exceed NH_3 concentrations (Figure 6). Additionally, the total amount of NO_X precursors is lower by a factor of about five compared to the large gasifier. Because the small gasifier tests were conducted without addition of limestone, it is not yet certain whether this reversal is caused by the anoxic (ER=0) operating condition or the absence of limestone, which might play a catalytic role.

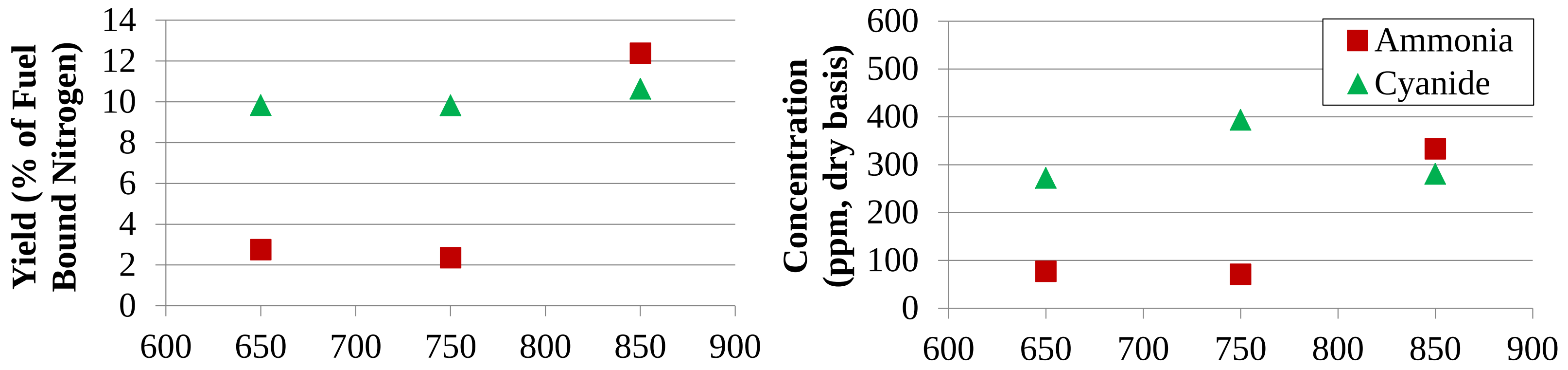

Figure 6. Percent yield and concentration data for NH_3 and HCN in syngas produced by the 100 g/h gasifier in response to changes in operating temperature.

Conclusions and Future Plans

- Our research confirms that for typical operating conditions for industrial gasifiers, NH_3 is the most important syngas nitrogen species [2-7]. However, we also found that HCN is a significant product, especially for herbaceous energy crops and waste feedstocks, which have far more FBN than woody feedstocks.
- Certain operating conditions, like those carried out in the small gasifier, can lead to yields of HCN that are greater than for NH_3. This contrasts with reports in the literature that indicate NH_3 is always the predominant nitrogen compound in syngas.
- Further work is needed to determine the mechanisms responsible for variations in the relative amounts of NH_3 and HCN in syngas.

Works Cited

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