



The role of char and tar in determining the gas-phase partitioning of nitrogen during biomass gasification



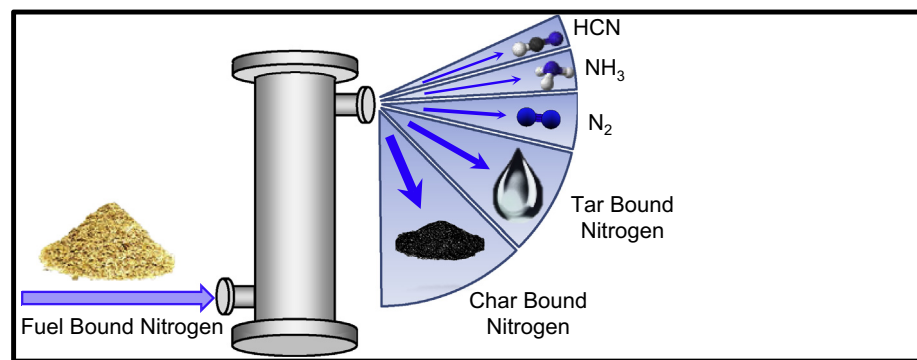
Karl M. Broer, Robert C. Brown*

Iowa State University, 1140E BRL, Ames, IA 50011-3270, USA

HIGHLIGHTS

- Switchgrass was gasified at an equivalence ratio of zero and 650–850 °C.
- Short residence times were employed to minimize secondary reactions.
- Char- and tar-bound nitrogen, NH₃, HCN, and N₂ were all significant products.
- Increasing temperature leads to increased release of gaseous nitrogen compounds.
- Kinetic models of gasification should include nitrogen release from char and tar.

GRAPHICAL ABSTRACT



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ABSTRACT

Gasification is an attractive option for converting biomass into fuels and chemicals. Most biomass contains significant amounts of fuel-bound nitrogen (FBN), which partially converts into ammonia (NH₃) and hydrogen cyanide (HCN) during gasification. These nitrogen compounds are problematic as they can lead to NO_x emissions or catalyst poisoning in downstream applications of syngas. FBN can convert to other products as well, including diatomic nitrogen (N₂), char-bound nitrogen (char-N), and tar-bound nitrogen (tar-N). Efforts to predict concentrations of NH₃ and HCN have been hindered by a lack of accurate, comprehensive measurements of nitrogen partitioning among gasification products. The present study gasified switchgrass under allothermal, short residence time conditions and measured NH₃, HCN, char-N, and tar-N as a function of temperature in the range of 650–850 °C with diatomic nitrogen determined by difference. It was found that a major portion of FBN was retained in the char and tar products. As temperature was increased, char and tar were consumed, releasing nitrogen as gaseous NH₃ and HCN. This increase in undesirable nitrogen compounds is contrary to the predictions of most gasification models, which overlook the presence of significant nitrogen in char and tar even if they include tar cracking and char gasification reactions. The results of this study demonstrate that gas-phase reactions alone are not sufficient to predict the fate of nitrogen during gasification. In order for modeling efforts to obtain more accurate predictions of nitrogen partitioning, the reactions through which gaseous nitrogen-bearing species are released from char and tar must be considered.

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* Corresponding author. Tel.: +1 515 509 0027.

E-mail addresses: kbroer@iastate.edu (K.M. Broer), rcbrown@iastate.edu (R.C. Brown).

1. Introduction

Gasification is a notable thermochemical conversion technology that can be used to transform carbonaceous solids into a variety of energy products including process heat, electrical power, and liquid transportation fuels. Gasification has advantages over biological conversion technologies in that it can efficiently utilize lignin and mixed wastes.

Most biomass feedstocks contain small amounts of nitrogen that mostly originate from protein, but also from nitrates, ammonium, chlorophyll, and nucleic acids. Nitrogen generally comprises a relatively small portion of the overall makeup of the biomass (0.05–2 wt% for most fuels) [1]. Nevertheless, fuel-bound nitrogen (FBN) has a large impact on syngas quality. Upon gasification, FBN transforms mainly into diatomic nitrogen (N_2), ammonia (NH_3), hydrogen cyanide (HCN), char-bound nitrogen (char-N), and tar-bound nitrogen (tar-N). Ammonia and HCN are the most problematic of these five forms. Both are precursors to NO_x formation during combustion of syngas for heat and power applications, which is a serious air pollutant [2]. Nitrogen in syngas is also a serious impediment to synfuels production applications because it poisons upgrading catalysts [3,4].

Herbaceous feedstock products such as miscanthus, switchgrass, wheat straw, and corn stover can easily contain over 0.5 wt% nitrogen, which is enough to generate NH_3 and HCN in concentrations on the order of 5000 ppm and 1000 ppm, respectively [5]. Much larger concentrations can be expected from gasification of some feedstocks such as grass clippings (2.47%) [6], sewage sludge (3.7–7.4%) [6–8], and *leucaena* (2.51%) [9]. When these fuels are gasified, dry basis concentrations of NH_3 in the syngas can easily exceed 10,000 ppm [6,7]. Most studies have found the yield of NH_3 to increase with gasification temperature. Rosén [10] gasified birch wood in air and found that NH_3 increased from 0–13% to 32–57% (FBN basis) as gasification temperature increased from 700 °C to 900 °C. Small increases in NH_3 yield were also observed by Vriesman et al. [11] as gasification temperature increased from 700 °C to 800 °C.

Hydrogen cyanide data are sparsely available in the literature, but most researchers report that the yield of HCN from biomass gasification is less than for NH_3 [12–14]. There are a few compelling examples, though, where HCN yields are reported to be higher than NH_3 . For example, Abelha et al. [8] gasified sawdust at 700–900 °C with an ER of zero in a 300 g/h fluidized bed reactor. HCN yields from FBN increased rapidly with temperature, reaching 47% at 900 °C. Such yields are remarkably high, translating to around 20,000 ppm dry basis for air gasification of a high nitrogen content feedstock. HCN yields on the order of 1–15% of the FBN are more typical, but the results of Abelha et al. [8,15] and others [12–14] support the contention that HCN is usually a significant nitrogen product in syngas. The difficulty of measuring HCN has obscured its importance in gasification and limited the number of studies that reliably report it [16].

Researchers have attempted to predict concentrations of some nitrogenous products of gasification using chemical kinetic models [12,13,17,18]. Most published models have been successful in predicting NH_3 over small ranges of operating conditions and for selected fuels, but they have significant limitations when applied to wider operating ranges and more diverse feedstocks. Modeling efforts to predict HCN, char-N and tar-N are rare due to the perception that they play minor roles in biomass gasification.

One of the most challenging aspects of chemical kinetic modeling is determining initial conditions for gas–phase and gas–solid reactions after the biomass has devolatilized, particularly for nitrogen-bearing compounds. Most models do not simulate nitrogen in its fuel-bound form since these chemical structures are

complex, heterogeneous, and not thoroughly understood. Instead, the primary gaseous products of pyrolysis are taken as the initial composition of the reacting gas mixture. These initial conditions are frequently assumed or sometimes estimated from devolatilization experiments performed in the absence of gaseous oxygen (O_2) [13,17,18]. de Jong et al. [12] employed an analytical model to estimate devolatilization of nitrogen species based on experiments in a thermogravimetric analyzer coupled to a Fourier Transform Infrared Spectrometer (TG–FTIR). Although this second approach offered better predictions of light gaseous nitrogen species, char-N and tar-N were not modeled.

After determining devolatilization products, the models used either global reaction schemes [17,18] or elementary reaction networks [12,13] to model homogenous reactions of the low molecular weight gas phase species. Elementary reaction networks tend to be well developed and include many different species. Rate parameters for global and fundamental reactions of simple carbon, oxygen, hydrogen, and nitrogen species have been widely published in the combustion literature, and have been useful in modeling gasification reactions [19,20].

It is much more difficult to model evolution of the char and tar. Models generally contain relatively few char and tar reactions compared to the homogeneous gas chemistry. There is also much less agreement on the proper mechanisms and rate parameters for the reactions in which tar and char participate. Tar is typically dealt with by referencing literature to determine how much tar might be produced by primary pyrolysis, and then assuming it undergoes a single step secondary cracking reaction that converts it to a few common carbon-, oxygen-, and hydrogen-bearing species. To model char gasification, the char yield from primary pyrolysis is used as an initial condition, and then char destruction rates are modeled via char combustion and gasification reactions. These reactions are usually assumed to be mass transfer limited, and therefore depend on char particle physiochemical properties. Models can also include reactions catalyzed by the char, which follow similar mass transfer limited reactions. In summary, uncertainties about the exact properties of the char and tar make it difficult to model the reactions in which they participate.

These difficulties have often deterred modelers from considering the possibility that significant amounts of nitrogen might be bound in the char and tar. Among the four kinetic models presented by Chen et al. [17], Liu and Gibbs [18], and de Jong et al. [12,13], tar-N was neglected by all four studies while char-N was considered by only Chen et al. [17] and Liu and Gibbs [18]. Experimental literature does not support the exclusion of char-N and tar-N reactions. Yields of char-N reported by Zhou et al. [9] and Yu et al. [21] were below 10%, but Vriesman et al. [11] reported much higher yields (14.0–21.0%). The char-N yield results of Abelha et al. [15] for gasification of *Cynara cardunculus* (Cardoon) are the highest (12% and 32%). The results of Abelha et al. [15] may be particularly relevant toward indicating yields of char-N immediately after devolatilization because residence time was short (approximately 2 s), and the reactor was operated in the absence of O_2 (ER = 0). These conditions would tend to produce char-N yields more representative of the devolatilization products than the other studies since the lack of O_2 and residence time would have minimized char oxidation and gasification reactions.

Measurements of tar-N yields in the literature are rare. The few that are available give conflicting evidence of whether tar-N produced by devolatilization of biomass is significant or not. Yu et al. [21] reported yields of tar-N from two woody feedstocks and two herbaceous feedstocks to be low (0.37–1.3% of FBN). Kurkela et al. [14] also reported low tar-N yields for straw gasification (0.8–1.8% of FBN). While these results seem low enough to neglect tar-N in modeling reactions of FBN, the gasification conditions in

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