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# A review on biomass gasification syngas cleanup

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## HIGHLIGHTS

- The study reviews biomass syngas cleanup technologies and R&D status.
- In-depth synthesis of gas cleanup to remove major syngas contaminants is provided.
- Contaminants of focus are tar, $NH_3$, HCN, $H_2S$, COS, halides (HCl) and trace metals.
- Major technical barriers related to gas cleanup are discussed.

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## ABSTRACT

Energy, fuel and chemical production from biomass is increasingly attracting interest in the world. Gasification of biomass can produce raw syngas which contains CO, $CO_2$, $H_2$ and $CH_4$. In addition, raw syngas contains minor but significant quantities of undesirable impurities – collectively known as syngas contaminants. Syngas contaminants are composed of tars, nitrogen based compounds ($NH_3$, HCN, etc.), sulfur based compounds ($H_2S$, COS, etc.), hydrogen halides (HCl, HF, etc.) and trace metals (Na, K, etc.). Raw syngas cleanup is an essential step prior to syngas utilization in downstream applications. In recent years, significant research attention has been devoted to syngas cleanup to reduce contaminants below tolerable limits. The present paper is a comprehensive review of cold gas and hot gas syngas cleanup for major contaminants in syngas (tar, $NH_3$, $H_2S$, HCl and trace metals). This review organizes and discusses investigations on syngas for all major contaminants, critically reviews important challenges in syngas cleanup and discusses recent advancements in hot and cold gas cleanup.



**Contents**



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## 1. Introduction

In the context of gasification, the term "contaminant" is used to refer to particulates, condensable organic compounds collectively known as tar, nitrogenous compounds like ammonia ($NH_3$) and hydrogen cyanide (HCN), sulfur containing inorganic compounds like hydrogen sulfide ($H_2S$), carbonyl sulfide (COS) and carbon disulfide ($CS_2$), hydrogen halides and halogens such as hydrogen chloride (HCl) and chlorine (Cl), and trace metals like sodium (Na) and potassium (K). These contaminants emanate from volatile organic and inorganic constituents in biomass and are consequently present at widely varying concentrations in syngas.

In general, tars are considered as all organic compounds with molecular weight greater than benzene as defined by a panel of experts of EU/IEA/US-DOE in 1998 [1]. As such, the definition of tar engulfs a wide range of compounds including oxygenates, phenolic compounds and olefins, aromatic and polyaromatic hydrocarbons (PHA) [2]. Relative to other contaminants, tar is the most abundant per unit weight of biomass gasified and has been the focus of the majority of contaminant remediation studies [3]. Its concentration in syngas depends on the feedstock, process conditions and the type of gasifier with lower oxygen supply and temperature resulting in higher tar concentration.

Nitrogen in biomass is converted to ammonia ($NH_3$), hydrogen cyanide (HCN), oxides of nitrogen (NO, $NO_2$, $N_2O$ and other $NO_x$) and $N_2$ [4]. However, among all deleterious nitrogenous species in biomass gasification product gas, $NH_3$ is the most abundant with concentrations between 350 and 18,000 ppmv depending on the nitrogen content in the feedstock [4–6]. The partition of biomass nitrogen favors $NH_3$ at temperatures below 800 °C with more than 60% by weight of the initial nitrogen in biomass converted to $NH_3$ [4]. However, as temperature is increased without additional oxygen supply, $N_2$ becomes the most dominant species from biomass nitrogen [4]. HCN and NOx are generally a smaller fraction of biomass nitrogen [4,6–8].

Sulfur in the biomass is converted primarily to hydrogen sulfide ($H_2S$), carbonyl sulfide (COS), carbon disulfide ($CS_2$) and other minor sulfur containing compounds with $H_2S$ being the most dominant [9]. $H_2S$ is typically present at concentrations less or near 100 ppmv for most woody and herbaceous biomass [10,11]. Halogens, like chlorine, and trace metals are released as hydrogen halides, such as hydrogen chloride (HCl), and as their respective salts by binding to metals in biomass such as alkali metals. Among these species, HCl and alkali metals (Na, K) are the most abundant hydrogen halides and metals, respectively for woody or herbaceous biomass [12]. It is noteworthy to indicate that the relative abundance and prevalence of specific contaminants can change drastically depending on the concentration of individual precursors (i.e. N, S, halogens and metals) in biomass as well as operating conditions.

The presence of these contaminants in syngas poses several technical and operational issues ranging from equipment corrosion ($H_2S$) and fouling (tar), catalyst deactivation (tar, $H_2S$, $NH_3$, HCl and trace metals) to environmental pollution ($NH_3$) [5,6,12]. As shown in Table 1, most downstream applications have very stringent requirements for syngas cleanliness with varying levels of cleanup demands depending on the application. Therefore, contaminant levels must be decreased by gas cleanup to adhere to the requirements of downstream applications [13].

Few comprehensive reviews on gas cleanup have been published in recent years. Woolcock and Brown presented an extensive and comprehensive review of cleanup technologies for cold, warn and hot gas cleanup for all major contaminants [13]. Others have summarized hot gas catalytic or sorbent removal of tar [15–17], hydrogen sulfide [17,18], ammonia [18] and catalytic conditioning of biomass-derived syngas [19]. The present review updates and complements those past reviews by extending the review to halides and trace metals that have previously only received limited attention and cold gas cleanup. However, this review does not cover particulate removal technologies which have been covered by a recent review [13]. Furthermore, this review critically discusses important challenges in syngas cleanup and discusses recent advancements in hot gas cleanup. Finally, existing barriers and the path forward to advance syngas cleanup are discussed.

## 2. Cold gas cleanup

Cold gas cleanup is commonly considered the conventional approach in syngas cleanup due to its proven reliability and high contaminant removal efficiency. The main distinguishing characteristic of this approach is that it is carried out at low temperature,

**Table 1**
Upper limits of contaminants in gasification syngas for selected applications [14].

| Applications | Tars (mg/N m$^3$) | Sulfur contaminants (ppmv) | Nitrogen contaminants (ppmv) | Alkali (ppmv) | Halides (ppmv) |
|---|---|---|---|---|---|
| Gas turbine | n/a | <20 | <50 | <0.02 | <1 |
| FT synthesis | <0.1–1[a] | 0.01 | 0.02 | 0.01 | 0.01 |
| Methanol synthesis | <1 | <1[b] | 0.1[b] | n/a | 0.1[b] |

n/a means not available.
[a] Units are in ppmv.
[b] Units in mg/N m$^3$.