



IEA Bioenergy
Technology Collaboration Programme

Gas Cleaning from Gasification for Production of Biofuels and Biochemicals

Review

IEA Bioenergy: Task 33

March 2025



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Abstract

During the thermochemical gasification process, the resulting gas, known as producer gas (or raw gas) must be cleaned before it can be utilized in applications such as combined heat and power production or advanced synthesis processes like biofuel and bio-based chemical production. This review focuses on characterizing the impurities and undesirable components present in producer gas, along with their separation methods. Special attention is given to tar, nitrogen, sulphur, and chlorine compounds, as these elements can disrupt downstream processes, leading to issues such as slagging, fouling, and catalyst poisoning, all of which negatively impact process operability and reliability.

Several factors influence the formation of undesirable components during gasification, with feedstock quality being one of the most critical. Additionally, process conditions such as temperature, pressure, heating rate, oxidizing ratio, and the feedstock's residence time in the reactor play significant roles in determining the composition of these unwanted byproducts.

Following the cleaning and conditioning stages, producer gas is upgraded to synthesis gas, or syngas. This refined gas is versatile and can be used in various applications. It can be combusted in internal combustion engines or gas turbines to produce heat and electrical power. Beyond energy generation, syngas serves as a key feedstock for several chemical synthesis processes, including the production of synthetic natural gas, the Fischer-Tropsch process for liquid fuels, hydrogen, methanol synthesis, and further products.

Each of these synthesis processes imposes strict requirements on syngas purity. Impurities such as sulphur, tar, particulates, and other contaminants must be controlled within specified limits to avoid catalyst poisoning, inefficiencies, or equipment damage during processing. These permissible impurity levels are critical for ensuring the effectiveness and longevity of the systems involved and vary depending on the specific catalytic process or chemical conversion being targeted.

This report presents a review of syngas cleaning technology. Chapter 1 focuses on formation and identification of contaminants, while Chapter 2 outlines the current state of gas cleaning methods, beginning with the removal of particulate matter, metals, and tar, followed by the elimination of sulphur, ammonia, and chlorine. The review concludes with an examination of recent advancements in gas cleaning technologies, with a focus on innovative methods for selectively optimizing syngas quality. These cutting-edge approaches aim to enhance the efficiency and effectiveness of gas purification and conditioning processes.

It is important to note that the field of gas cleaning and conditioning for synthesis processes is continually evolving. Ongoing research and technological advancements are expected to drive further innovations, offering new solutions and improvements to meet the ever-increasing demands of industrial applications.

Introduction

When a carbonaceous feedstock such as biomass is gasified to make synthesis gas (syngas; a mixture of hydrogen and carbon monoxide), undesirable byproducts are also produced that must be reduced or eliminated depending on the end use of the syngas. These include both solids in the form of char particles and fly ash and gaseous and vapor-phase species such as hydrogen sulfide (H₂S), carbonyl sulfide (COS), ammonia (NH₃), hydrogen cyanide (HCN), hydrochloric acid (HCl), and vapor-phase tar species.¹

Solids such as residual carbon and/or alkali and alkaline earth metals must be removed for almost any process, and catalytic syngas conversion processes require some or all of these impurities to be removed upstream of the conversion reactor. There are a number of journal articles that have reviewed syngas cleaning and/or reported on new techniques for removing contaminants.² In this publication, we synthesize these reports and provide an update on the state of technology for syngas cleaning, where extensive removal of contaminants to very low levels are required due to stringent downstream processing limitations.

The steps of gas cleaning can be summarized as follows (processes that can be used are summarized in Chapter 2):

1. Removal of Particulates

- **Cyclones and Filters:** Initial cleanup involves the use of cyclones and bag filters to remove particulate matter (PM). Cyclones use centrifugal forces to separate larger solid particles, while bag filters capture fine solid particulates.
- **Ceramic or Metal Filters:** At higher temperatures, ceramic or metal filters can be employed to trap finer particles that may have passed through the initial stages such as cyclones.

2. Tar and Hydrocarbon Removal

- **Thermal Cracking:** High-temperature processes can crack tars and heavy hydrocarbons into lighter compounds.
- **Catalytic Cracking:** Catalysts such as nickel-based or dolomite can be used to facilitate the cracking of tars at lower temperatures.

3. Desulphurization

- **Absorption:** Sulphur compounds such as H₂S are removed using sorbents. This process can occur at high temperatures (hot gas cleanup) or lower temperatures (cold gas cleanup).
- **Zinc Oxide Sorbents:** Solid sorbents, such as zinc oxide, can also be used to react with H₂S to form zinc sulfide, thereby removing sulphur from the syngas.

4. Removal of Chlorides and Ammonia

- **Wet Scrubbing:** Chlorides and ammonia can be effectively removed using wet scrubbers, where the syngas is passed through a liquid solution that absorbs these contaminants.
- **Solid Sorbents:** Solid sorbents such as activated carbon can also be used to capture chlorides and ammonia.

¹ Tars may be defined as condensable hydrocarbons that are formed by the thermal breakdown of organic macromolecules in biomass (cellulose, hemicellulose, and lignin) and are generally above benzene in molecular weight.

² Abdoulmoumine, N., Adhikari, S., Kulkarni, A., & Chattanathan, S. (2015). A review on biomass gasification syngas cleanup. *Applied Energy*, 155, 294-307.
<https://doi.org/10.1016/j.apenergy.2015.05.095>

5. Carbon Dioxide (CO₂) Removal

- **Physical and Chemical Solvents:** CO₂ can be removed using solvents like Selexol (a physical solvent) or chemical solvents such as amines. Physical solvents are more effective at higher pressures, while chemical solvents are preferred for their higher selectivity.
- **Pressure Swing Adsorption (PSA):** This method employs adsorbent materials to capture CO₂ under high pressure and then release it upon depressurization.

6. Mercury Removal

- **Activated Carbon:** Mercury can be adsorbed onto activated carbon, which is often impregnated with sulphur to enhance its capture efficiency.
- **Metal Sulfides:** Metal sulfide sorbents, such as those containing copper or zinc, can also be employed to capture mercury.

7. Final Polishing

- **Guard Beds:** Guard beds filled with specific adsorbents are used in the final stage to remove trace amounts of remaining contaminants, ensuring the syngas is of high purity before utilization.

Conversion processes that can use syngas to produce value-added products include the well-known Fischer-Tropsch synthesis for production of a wide variety hydrocarbons (diesel, gasoline, waxes). Hydrogen can be produced from the syngas through the steam reforming and water - gas shift reactions. Methanol is produced from synthesis gas by the hydrogenation of carbon oxides over a suitable catalyst. The syngas could be used to produce mixed alcohols, methane or renewable natural gas (SNG), hydrogen, and electricity via either direct combustion of syngas or via solid oxide fuel cells. All of these conversion processes require a syngas cleanup process that essentially reduces most of the impurities to very low levels. Table 1 presents the level of deep cleaning required for Fischer-Tropsch applications where cobalt and iron catalysts are used. Generally, these levels are similar to the requirements for the other chemical conversion processes. The nickel-based catalyst utilized in synthetic natural gas production requires less than 0.2 ppm of total sulphur entering the methanation reactor, along with total removal of the hydrocarbons and other contaminants such as HCN and ammonia. The nickel-based anode in the solid oxide fuel cell must have sulphur removed to sub-parts-per-million levels along with the removal of other contaminants such as phosphine, arsine, antimony, cadmium, and chlorine. Trace hydrocarbons such as benzene have been shown to lead to carbon deposition in the solid oxide fuel cell anodes and must be controlled. Maximum contaminant levels for these impurities entering a solid oxide fuel cell stack have not been determined but are expected to be in the low parts-per-million range.

Table 1: Summary of Effect of Poisons on Performance of Fe and Co Catalysts

Catalyst Type	Fe, 270°C, 1.3 MPa, H ₂ /CO 0.67, Conv. 40 %		Co, 220°C, 2.0 MPa, H ₂ /CO 2.0, Conv. 80 %	
	Limit, ppm	Impact	Limit, ppm	Impact
NaCl	100	Minor	50	Minor
KCl	20	Negligible	100	Minor
NaHCO ₃	40	Negligible	1,000	Negligible
KHCO ₃	40	Negligible	1,000	Negligible
HCl	20	Major	20	Moderate
HBr	20	Major	20	Moderate
HF	20	Major	1	Major
NH ₃	200	None	100	Moderate
H ₂ S	0.3	Major	1	Major
HCN	6	Minor	10	Moderate

Key Considerations

- **Efficiency and Cost:** The choice of cleanup technologies depends on the syngas composition, the required purity levels, and economic considerations. Combining multiple cleanup stages often yields the best results.
- **Environmental Impact:** Proper handling and disposal of spent sorbents and other waste materials generated during the cleanup process are crucial to minimize environmental impact.

1. Overview on Impurities in the Gas Phase: Feedstock Dependence and Gasification Technologies

1.1. IMPURITIES IN THE GAS PHASE

The gasification process encounters certain commercialization challenges attributed to the presence of pollutants within the product gas. The presence of organic compounds, alkali, alkali earth, and ash- and slag-forming components can result from contaminants in biomass and waste feedstocks used and process conditions used for the gasification reaction itself. Alkali and alkaline earth metals and other inorganic components are usually present in various organic structures, minerals, and salts within the feedstocks. During the process of gasification, these organic materials undergo thermal degradation resulting in their release in product gases, tars, and residual carbon (char).

The presence of chlorine, sulphur, and organic salts in the feedstock can lead to two possible outcomes: either these elements bind with the ash and char, resulting in their discharge as solid residue, or they adhere to or combine with particulate matter and tars, becoming pollutants that are carried along with the syngas. The presence of these pollutants has the potential to cause fouling and corrosion in downstream equipment, as well as to adversely affect the performance of catalysts through their toxic properties. Therefore, it is crucial to exercise control over these chemicals present in the syngas for the subsequent processes.³

The existence of these contaminants in the feedstock and in the resulting producer gas is a notable obstacle in terms of operational efficiency and requirements for capital expenditure for biomass gasification. This chapter discusses the factors that contribute to impurities formation during gasification, such as composition of the biomass feedstock and the applied gasification technology.⁴ The impurities to be described include tars, nitrogen- and sulphur-containing impurities, halides, and trace metals.

1.1.1. Tars

Tar is a generic term that describes a complex mixture of condensable hydrocarbon vapours. Tars from biomass gasification are represented by a thick, brownish-black, highly viscous compound that comprises complex polycyclic hydrocarbons, single- to multi-ring aromatic compounds, and other oxygen-containing hydrocarbons.⁵ The Gasification Task of the IEA Bioenergy Agreement, the U.S. Department of Energy, and the the Directorate General for Energy of the European Commission agreed to define tar as 'hydrocarbons with molecular weight greater than benzene'.⁶

In the literature, two distinct classification approaches for tars have been broadly defined. The first was described by Evans and Milne, who divided tar compounds into four lumps as shown in Figure 1.

³ AECOM & Fichtner Consulting Engineers. (2021). Advanced Gasification Technologies - Review and Benchmarking: Review of current status of advanced gasification technologies. BEIS Research Paper Number 2021/038. <https://assets.publishing.service.gov.uk/media/615ec02be90e07197867ea85/agt-benchmarking-task-2-report.pdf>

⁴ Rabou, Luc P. L. M. et.al., 2009, 'Tar in Biomass Producer Gas, the Energy research Centre of the Netherlands (ECN) Experience: An Enduring Challenge' Energy Fuels, 23, 12, 6189-6198. <https://doi.org/10.1021/ef9007032>.

⁵ Font Palma, C. (2013). Modelling of tar formation and evolution for biomass gasification: A review. Applied Energy, 111, 129-141. <https://doi.org/10.1016/j.apenergy.2013.04.084>.

⁶ Maniatis, K., & Beenackers, A. A. C. M. (2000). Tar protocols. IEA Bioenergy Gasification Task. Biomass & Bioenergy, 18(1), 1-4. [https://doi.org/10.1016/S0961-9534\(99\)00081-2](https://doi.org/10.1016/S0961-9534(99)00081-2)

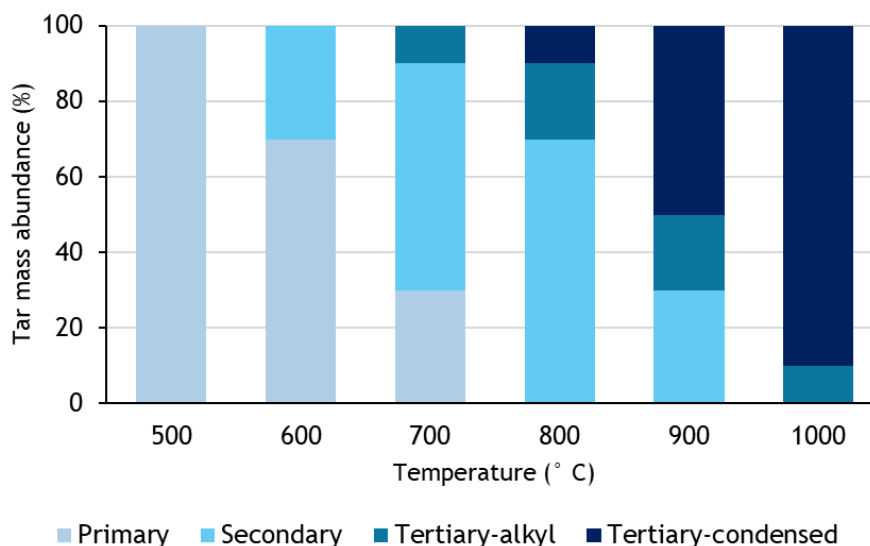


Figure 1: Primary, secondary, and tertiary tar formation 500°C-1,000°C temperature range (Adapted from⁷)

In this approach, tars are categorized based on their reactivity and molecular structure. Primary tars are derived from oxygenated products formed at temperatures between 400°C and 700°C, such as syringols and furans. Secondary tars include products such as phenolics and olefins evolving from the primary tar phase at temperatures between 700°C and 850°C. Tertiary tars consist of polyaromatic hydrocarbons formed at temperatures between 850°C and 1,000°C, such as toluene and indene.⁸

The second approach, from the Energy Research Centre of the Netherlands (ECN), proposed a tar classification scheme that divides tar chemicals into five groups (light aromatics, heterocycles, light and heavy polyaromatic hydrocarbons, and gas chromatography undetectable tar), depending on their molecular weight, solubility, and condensability. Depending on the intended use, both tar classifications approaches are frequently employed and are complementary. Table 2 summarizes both approaches.⁹

⁷ Evans, R. J., & Milne, T. A. (1997). Chemistry of tar formation and maturation in the thermochemical conversion of biomass. In A. V. Bridgwater & D. G. B. Boocock (Eds.), *Developments in Thermochemical Biomass Conversion* (pp. 803-816). Springer. https://doi.org/10.1007/978-94-009-1559-6_64.

⁸ Rakesh N, Dasappa S. 2018, 'A critical assessment of tar generated during biomass gasification - formation, evaluation, issues and mitigation strategies. *Renew Sustain Energy*; 91:1045-64. <https://doi.org/10.1016/j.rser.2018.04.017>

⁹Cortazar, M. L., et al. (2023). A comprehensive review of primary strategies for tar removal in biomass gasification. *Energy Conversion and Management*, 276, 116496. <https://doi.org/10.1016/j.enconman.2022.116496>.

Table 2: Tar Classification Methods, Properties, and Typical Compounds⁵

Classification Method	Basis of Classification	Type	Description	Properties	Typical Compounds
Milne et al.	Reactivity, appearance	Primary	Cellulose-, hemicellulose-, and lignin-derived oxygenated compounds	Low-molecular-weight oxygenated hydrocarbons	Acids, sugars, alcohols, ketones, aldehydes, catechol, guaiacol, anisole, vanillin
		Secondary	Product from the conversion of primary products (phenolic and olefin compounds)	Alkyl phenols	Phenol, cresol, xylene
				Single-ring aromatics	
		Alkyl tertiary	Aromatic compounds with methyl branches	Methyl-derivative aromatics with one or more rings	Methyl acenaphthylene, methyl naphthalene, toluene, indene
Condensed tertiary	Polycyclic aromatic compounds without branches	Polynuclear aromatic hydrocarbon series without substituents	Benzene, naphthalene, acenaphthylene, anthracene, phenanthrene, pyrene		
ECN-TNO-UT	Molecular weight, solubility, and condensability	Class I	Gas chromatography undetectable compounds	Very heavy compounds with 8 or more rings	
				Not detected by gas chromatography	
				Calculated by subtracting the gas chromatography detectable tar from the total gravimetric tar	
		Class II	Heterocyclic compounds	Single-ring aromatics containing heteroatoms	Pyridine, phenol, cresol, quinoline, isoquinoline
				High solubility in water	
		Class III	Light aromatic compounds	Single-ring aromatic compounds	Toluene, ethylbenzene, xylenes, styrene
				Without condensability and solubility problems	
		Class IV	Light polyaromatic hydrocarbons	2-3-ring aromatic compounds	Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthylene, fluorene, phenanthrene, anthracene
				Condense at low temperatures	
		Class V	Heavy polyaromatic hydrocarbons	More than 3-ring aromatic compounds	Pyrene, fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, benzo(k)fluoranthene
Condense at very low temperatures					

Tar formation is influenced by a range of complex reactions, with its occurrence being highly dependent on factors such as the composition of the feedstock, the design of the reactor, and the gasifier operational parameters. Moreover, the presence of lignin in biomass exerts a significant effect on the formation of tar and the generation of hazardous compounds.¹⁰ To prevent the formation of tar, it is crucial to consider the biomass feedstock being used, as an analysis of the feedstock composition facilitates the identification of the specific components that will contribute to tar formation.

As normally practiced, the process efficiency is decreased by 5 % to 15 % due to tar production, which wastes some of the energy produced during biomass gasification. In the product gas, all tar compounds are undesirable because they could condense or polymerize into more complex structures on downstream pipelines, heat exchangers, or filters, causing corrosion, fouling, and clogging.¹¹ As a result, emissions and operational expenses rise, and both process efficiency and overall carbon efficiency decline. For these reasons, the industrial feasibility of the gasification process has been hampered by the presence of tars, and projects have been abandoned as a result of the technical and financial challenges related to its presence in producer gas.¹² Most technologies and R&D on tar mitigation are concentrated around tar transformation by catalytic or thermal cracking, which helps reduce high-molecular-weight tars and increase the calorific value of the producer gas, or catalytic reforming that improves carbon efficiency by producing additional syngas from tars.

1.1.2. Nitrogen-Containing Impurities

Biomass gasification applied for sustainable energy production can be extremely challenged due to nitrogen-containing contaminants present in the produced gas stream.¹³

The nitrogen content in biomass and other waste carbon feedstocks varies widely by the feedstock source. Nitrogen-rich fertilisers, animal dung, peat, and irrigation wastewater are potential nitrogen sources in biomass feedstocks due to the presence of proteins in the feedstock. Nitrogen-containing syngas contaminants include amines, amides, and nitriles, all of which may cause operational and environmental issues during and after gasification. The most significant species from nitrogen conversion in biomass gasification are ammonia (NH₃) and hydrogen cyanide (HCN), which are the principal precursors of nitrogen oxide emissions (NO_x) in downstream burners, gas engines, or gas turbines. The amount of nitrogen pollutant emitted during gasification is strongly influenced by intrinsic feedstock qualities (total nitrogen content and functionality) and process parameters. When biomass with relatively high nitrogen content is gasified, it produces a product gas with NH₃ contents ranging from 500 to 30,000 ppm,^{14,15} whilst the NH₃-to-NO_x conversion can be as high as 50 % when the gasification gas stream is burned to generate electricity. Legal environmental restrictions have imposed stronger limits on NO_x emissions, making NH₃ removal a priority.¹⁶ Nitrogen is released from protein structures or heterocyclic aromatic

¹⁰ Yu, H., Zhang, Z., Li, Z., & Chen, D. (2014). Characteristics of tar formation during cellulose, hemicellulose and lignin gasification. *Fuel*, 118, 250-256. <https://doi.org/10.1016/j.fuel.2013.10.080>.

¹¹ Qin, Y., Campen, A., Wiltowski, T., Feng, J., & Li, W. (2015). The influence of different chemical compositions in biomass on gasification tar formation. *Biomass and Bioenergy*, 83, 77-84. <https://doi.org/10.1016/j.biombioe.2015.09.013>

¹² A. Gredinger, R. Spörl, G. Scheffknecht, (2018), Comparison measurements of tar content in gasification systems between an online method and the tar protocol, *Biomass Bioenergy*, 111, pp. 301-307.

¹³ Pröll, T., Siefert, I. G., Friedl, A., & Hofbauer, H. (2005). Removal of NH₃ from biomass gasification producer gas by water condensing in an organic solvent scrubber. *Industrial & Engineering Chemistry Research*, 44(5), 1576-1584. <https://doi.org/10.1021/ie049669v>

¹⁴ Torres W, Pansare SS, Goodwin JG. Hot gas removal of tars, ammonia, and hydrogen sulphide from biomass gasification gas, *Catal Rev*, 2007, vol. 49 (pg. 407-56)

¹⁵ Zhou J, Masutani SM, Ishimura DM, et al. Release of fuel-bound nitrogen during biomass gasification, *Ind Eng Chem Res*, 2000, vol. 39 (pg. 626-34)

¹⁶ Zhang, W., Dong, L., & Zhang, M. (2012). Gas cleaning strategies for biomass gasification product gas. *International Journal of Low-Carbon Technologies*, 7(2), 69-74. <https://doi.org/10.1093/ijlct/ctr046>

compounds in the feedstock during the pyrolysis stage of gasification and combustion.¹⁷ Figure 2 shows how the content of lignin and protein affects the formation of these chemicals by comparing rice straw, leaves and wood against soybean. During the pyrolysis step, if there is more protein in biomass, the release of NH₃ will dominate the formation of HCN; if there is more lignin present in the biomass composition, the effect will be the opposite, favouring the HCN formation over NH₃.

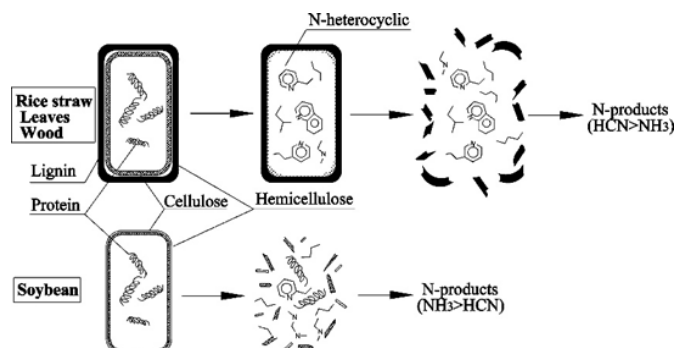


Figure 2: Processes of nitrogen release during the pyrolysis experiments¹⁷

Ammonia can be produced directly from biomass in primary processes or indirectly from HCN in secondary gas-phase reactions. Secondary reactions can increase the concentration of HCN and NH₃ when the temperature rises due to feedstock conversion. Increased H₂ availability and residence time, on the other hand, will convert HCN to NH₃. Given enough time and temperature, N₂ is the dominating equilibrium product, but this is rarely achieved in practice.¹⁸ The distribution of fuel nitrogen into gasification products, using different feedstocks and process conditions, is shown in Table 3. This table clearly indicates that ammonia is the main fixed nitrogen compound, and fuel nitrogen conversion to HCN is remarkably lower when compared to fuel nitrogen conversion to ammonia. This study reported the main nitrogen-tar compound identified to be pyridine with small concentrations of pyrrole, quinazoline, and quinolines. Low ammonia concentrations are observed.¹⁹

Table 3: Typical NH₃ and HCN Contents in Product Gas in Fluidised-Bed Air Gasification¹⁷

Parameter	Pine Sawdust	Pine Chips	Pine Bark	Forest Residues	Wheat Straw
Pressure (MPa)	0.5	0.5	0.5	0.5	0.5
T (bed), °C	831	900	891	914	670
T (freeboard), °C	968	906	950	943	830
Bed additive	Dolomite	Dolomite	Dolomite	Dolomite	Al ₂ O ₃
Concentrations in Wet Gas (ppm by volume [ppmV])					
NH ₃	314	915	1,418	2,104	2,410
HCN	8	36	54	78	350
Fuel-N Conversion (wt %)					
To NH ₃ -N	72	75	67	65	60
To HCN-N	1.7	2.9	2.5	2.4	8.8

¹⁷ Hansson, K.-M., Samuelsson, J., Tullin, C., & Åmand, L.-E. (2004). Formation of H₂CO, HCN, and NH₃ from the pyrolysis of bark and nitrogen-containing model compounds. *Combustion and Flame*, 137(3), 265-277. <https://doi.org/10.1016/j.combustflame.2004.01.005>.

¹⁸ Woolcock, P. J., & Brown, R. C. (2013). A review of cleaning technologies for biomass-derived syngas. *Biomass and Bioenergy*, 52, 54-84. <https://doi.org/10.1016/j.biombioe.2013.02.036>.

¹⁹ Kurkela, E 1996, 'Formation and removal of biomass-derived contaminants in fluidized-bed gasification processes: Licentiate thesis', Licentiate Degree, University of Jyväskylä, Espoo. <https://www.osti.gov/etdeweb/servlets/purl/442486>.

As mentioned previously, there are many deleterious impacts of nitrogen-containing contaminants on gasification performance and downstream applications. To mitigate the impact of nitrogen-containing impurities on gasification systems and ensure that the technology is used safely and efficiently, different measures such as the ones summarised in Table 4 can be implemented. Technologies for controlling and reducing the presence of nitrogen-containing compounds are reviewed in the next chapter of this report.

Table 4: Mitigation Measures to Reduce Negative Effects of Nitrogen-Containing Impurities on Gasification Systems¹⁷

Measure	Potential Benefit
Select biomass feedstocks with low levels of nitrogen	Biomass feedstocks with high levels of nitrogen should be avoided, if possible
Use gasifiers with high temperatures and pressures	Higher temperatures and pressures can help reduce the formation of NO _x
Install flue gas treatment systems	Flue gas treatment systems can be used to remove NO _x and other pollutants from the syngas
Use of catalyst	Catalysts can be used to remove impurities from the syngas, including nitrogen-containing compounds
Gasifier operation	Proper operation of the gasifier can help minimize the formation of nitrogen-containing compounds and other pollutants

Table 5 summarizes some catalysts that can be used to promote NH₃ conversion in different fuel gases.²⁰ To avoid toxic HCN emissions, catalytic oxidation or hydrolysis can be used downstream to promote Reactions 1 and 2 below, respectively.^{21,22} HCN can also be removed via selective catalytic reduction using active catalysts such as CuSO₄/TiO₂, although care should be taken on the associated N₂O emissions.²³

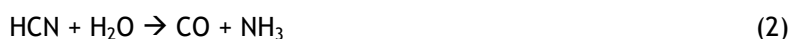


Table 5: Decomposition of Ammonia in Presence of Synthetic Fuels and Gasification Gases

Catalyst	Temperature, °C	Pressure, MPa	Fuel Gas	NH ₃ , ppm	
				In	Out
CaOMgO	900	0.1	H ₂	1,000	100
CaOMgO	1,000	0.1	H ₂ +CO+CO ₂ +CH ₄ +C ₂ H ₄	1,000	700
CaO	875	0.1	H ₂ +CO+CO ₂	3,000	2,100
Ni monolith	836/669	0.1	Gas from pinewood gasification	2,500	1,230
Ni based	900	1.5	Gas from sawdust gasification	400	50
Ni/Al ₂ O ₃	900	2.0	H ₂ +CO+CO ₂ +CH ₄ +C ₂ H ₄	2,100	350
			H ₂ +CO+CO ₂ +CH ₄ +C ₂ H ₄ +toulene		390

²⁰ Walter T., Sourabh S. P. James G. Goodwin Jr., (2007), Hot Gas Removal of Tars, Ammonia, and Hydrogen Sulphide from Biomass Gasification Gas, Catalysis Reviews, 49:4, 407-456, DOI: [10.1080/01614940701375134](https://doi.org/10.1080/01614940701375134)

²¹ Kröcher, O., & Elsener, M. (2009). Hydrolysis and oxidation of gaseous HCN over heterogeneous catalysts. Applied Catalysis B: Environmental, 92(1-2), 75-89. <https://doi.org/10.1016/j.apcatb.2009.07.021>.

²² Frilund, C., Tuomi, S., Kurkela, E., & Simell, P. (2021). Small- to medium-scale deep syngas purification: Biomass-to-liquids multi-contaminant removal demonstration. Biomass and Bioenergy, 148, 106031. <https://doi.org/10.1016/j.biombioe.2021.106031>.

²³ Miyadera, T. (1998) Selective reduction of NO_x by ethanol on catalysts composed of Ag/Al₂O₃ and Cu/TiO₂ without formation of harmful by-products. Applied Catalysis B: Environmental. 16:2: 155-164.

1.1.3. Sulphur-Containing Impurities

Sulphur is found in biomass in the form of organic sulphur and inorganic sulphates. The presence of these components in the feedstock is highly influenced by feedstock type; for biomass farming techniques, growing time and fertiliser types are significant. Initially released sulphur is primarily derived from the degradation of organic sulphur molecules found in proteins such as amino acids, cysteine, and methionine. Sulphur release in char combustion (often used as a source of heat for the primary gasifier) is primarily driven by the degradation and transformation of inorganic sulphates. Recent research reveals that internal biomass elements such as potassium, calcium, silicon, and chlorine can influence sulphur release.²⁴ The sulphur content of the agro-biomasses is known to vary and to be significantly different from woody biomass. For example, sulphur concentration of miscanthus is 0.55 %, whilst pine sawdust only has 0.01 %.²⁵

In gasification operations, sulphur can produce trace levels of thiophenes, mercaptans, and carbon disulfide (CS₂), as well as carbonyl sulfide (COS) and hydrogen sulfide (H₂S). During gasification, sulphur in biomass is transformed into H₂S via the shift reaction with COS (Reaction 3) and the reaction of organic sulphur with H₂ (Reaction 4):²⁶



H₂S formation can be promoted when active fluidized-bed technology is used along with steam gasification. Gasifiers using an inert bed produce more H₂S under air gasification, as shown in Table 6. Sulphur compounds are highly undesirable in the synthesis gas products if the process involves conversion of syngas to hydrocarbon transportation fuels using Fischer-Tropsch synthesis catalysts.²⁷ In addition, the presence of sulphur compounds can impact other gas cleaning processes such as those used for tar and ammonia abatement. This aspect holds significant importance in defining the gas cleaning sequence.²⁸ Iron catalysts exhibit a higher tolerance for sulphur compound concentrations compared to cobalt catalysts, with respective thresholds of 100 ppb and 60 ppb. A study conducted on a 500-hour run of a biomass-to-liquid process utilising a catalyst based on iron did not report any poisoning or loss of catalytic activity when subjected to concentrations of sulphur compounds below 1 ppmV.²⁹ A significant reduction in H₂S content in raw gases was achieved by employing a water scrubber, resulting in a decrease from 18 to 0.5 ppmV. Throughout this procedure, the concentration of COS remained constant at 1.2 ppmV.

Solid sorption techniques are suitable for the removal of small amounts of H₂S, using adsorbents such as iron oxide (about 1 ppmV), manganese oxide (approximately 5 ppmV), zinc oxide (less than 0.3 ppmV), copper oxide (less than 1 ppmV), and calcium oxide (approximately 50 ppmV). The operational temperature range typically falls within 350°C to 500°C, except for calcium and manganese, which can withstand temperatures of up to 1,000°C. Most sorbents currently lack the ability to be regenerated and hence require disposal after use. However, ongoing efforts are being made to create regenerative

²⁴ Suriyati Binti S., Toh, J., & Kuan, H. (2014). Release of chlorine and sulphur during biomass torrefaction and pyrolysis. *Energy & Fuels*, 28(6), 3738-3746. <https://doi.org/10.1021/ef4021262>.

²⁵ Wilen, C., Moilanen, A., & Kurkela, E. (1996). Biomass feedstock analyses. ESPOO.

²⁶ Kuramochi, H., Wu, W., & Kawamoto, K. (2005). Prediction of the behaviors of H₂S and HCl during gasification of selected residual biomass fuels by equilibrium calculation. *Fuel*, 84(3), 377-387. <https://doi.org/10.1016/j.fuel.2004.09.009>

²⁷ *E4Tech*, 20009 'Review of technologies for gasification of biomass and wastes - final report'.

²⁸ Long, R. Q., Monfort, S., Arkenberg, G., Matter, P., Swartz, S. L., & Lunsford, J. H. (2012). Sulfur tolerant magnesium nickel silicate catalyst for reforming of biomass gasification products to syngas. *Catalysts*, 2(2), 264-280. <https://doi.org/10.3390/catal2020264>

²⁹ Kim, K., Kim, Y., Yang, C., Moon, J., Kim, B., Lee, J., Lee, U., Lee, S., Kim, J., Eom, W., Lee, S., Kang, M., & Lee, Y. (2013). Long-term operation of biomass-to-liquid systems coupled to gasification and Fischer-Tropsch processes for biofuel production. *Bioresource Technology*, 127, 391-399. <https://doi.org/10.1016/j.biortech.2012.09.126>

procedures for these sorbents.

Table 6: H₂S Impurity Concentration Ranges for Biomass Gasification Producer Gases²⁶

Biomass	Bed material	Gasification Agent	Temperature, °C	mg/Nm ³
Pine	Inert (sand)	Air	790	32.56
		Air	934	37.54
		Air	1,078	40.79
Cynara/eucalyptus	Active (olivine/dolomite)	Steam	850	18.80
Pine	Active (ilmenite)		800–850	40.50
	Active (olivine)		800–860	52.50
	Inert (sand)		800–840	156
Almond shells	Active (olivine)		820–830	60
Wood	Inert (sand)	Air	850	150
Bark	Active (dolomite)	Steam	923	150
RDF ^a	Active (dolomite)	Air	859	195
Pine	Active (CaO)	Steam	780	36
Rice husk	Inert (sand)	Air	850	143
		Steam		255
Cacao shells	Inert	Air	822	30
Willow			827	75
Railroad ties			855	210
Park wood			861	345
SRF ^b			Active (olivine)	800
		850	891	

^a RDF: Refuse Derived Fuel; ^b SRF: Solid Recovered Fuel

COS is an organic sulphur compound that cannot be removed efficiently by physical or chemical removal processes. Thermodynamically, COS will shift toward formation of H₂S as the gas is cooled down to a low temperature; at a gas temperature of 200 °C no COS is present. Catalysts applied for this conversion include activated alumina, titania on alumina, and Mo/Co catalyst. The ZnS product from the absorption of H₂S with ZnO also catalyses the COS conversion via the hydrogenation reaction. So, when the ZnO bed contains ZnS, COS can be converted into H₂S, which is subsequently adsorbed by the ZnO. As such, an upstream catalyst for the removal of COS would not be necessary.³⁰

1.1.4. Hydrogen Halide and Trace Metals

In general, biomass and waste-derived feedstocks commonly consist of chlorine as the primary halogen, which undergoes a reaction with water vapour at high temperatures during the gasification process, resulting in the formation of HCl.^{31,32} Hydrogen chloride exhibits the highest concentration among chlorine

³⁰ van Paasen, S. V. B., Cieplik, M. K., & Phokawat, N. P. (2006). Gasification of non-woody biomass economic and technical perspectives of chlorine and sulphur removal from product gas (Non-confidential version) (Report No. ECN-E--06-032). Energy research Centre of the Netherlands.

³¹ IEA Bioenergy. (2018). Gas analysis in gasification of biomass and waste - Guideline report - Document 1. International Energy Agency. <https://www.ieabioenergy.com/wp-content/uploads/2018/09/IEA-Bioenergy-Task-33-gas-analysis-report-Document-1-1.pdf>

³² Recari, J., Berruero, C., Abelló, S., Montané, D., & Farriol, X. (2016). Gasification of two solid recovered fuels (SRFs) in a lab-scale fluidized bed reactor: Influence of experimental conditions on

compounds, rendering it the most significant in this regard, although other halides—namely NaCl and KCl, which are considered to be independent products derived from alkali metals—are also produced in minor concentrations. The concentration of HCl does not exhibit a linear relationship with the amount of chlorine present in the feedstock, as it is influenced by additional factors such as alkaline and alkali earth metals, as well as heavy metals.

The presence of steam can result in harm to stainless steel, thereby reducing the ash softening temperature and potassium mobility. Consequently, this can lead to fouling, slagging, and corrosion of metallic surfaces. Furthermore, if the gas is cooled to temperatures below 300°C–400°C, this can lead to the formation of alkali halide salts, particularly when there is an excess of alkalis compared to halides.^{33,34}

Both hydrofluoric acid (HF) and HCl are classified as strong acids due to their high degree of dissociation in water. Their solubility in water is further enhanced when the water is alkaline; as such, these compounds are commonly removed using wet scrubbers with either water or a caustic solution (NaOH in water).³⁵ Using caustic solution can also remove other compounds such as COS and CO₂. Hydrogen halides are commonly removed from syngas via dehydrohalogenation, for which alkaline and alkali earth metals can be promising halide sorbents when used at temperatures above 500°C.³⁶ Alkali metals (Li, Na, and K) can remove other halides such as HI and HBr, and when exposed to syngas with high CO₂ concentrations, alkali metal carbonates (e.g., Li₂CO₃) will be formed.³⁷ Alkaline earth metals (Mg, Ca, Sr, and Ba) can be used as HCl sorbents in their oxide form, with reported HCl removal capabilities BaO > SrO > CaO > MgO.

Metals can be removed together with halides, as alkali metals in the syngas combine with halides to form salts (e.g., KCl, NaCl); for this conversion, fly ash and bentonite as sorbents are efficient. Other sorbents such as kaolinite, bauxite, and zeolites are also effective aluminosilicate sorbents.³⁸

1.1.5. Contaminants Summary

The limits on the contaminants described above depend on the intended syngas application. A general guideline on the limits of these contaminants when considering gas turbine, Fischer-Tropsch synthesis, or methanol synthesis are shown in Table 7 for tars, sulphur components, nitrogen, alkali, and halides.

Table 7: Upper-Limit Contaminants for Syngas Selected Applications⁴³

Application	Tars (mg/Nm ³)	Sulphur (ppmV)	Nitrogen (ppmV)	Alkali (ppmV)	Halides (ppmV)
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process performance and release of HCl, H₂S, HCN and NH₃. Fuel Processing Technology, 142, 107-114.
<https://doi.org/10.1016/j.fuproc.2015.10.006>

³³ Gupta, R. P., & O'Brien, W. S. (2000). Desulfurization of hot syngas containing hydrogen chloride vapors using zinc titanate sorbents. Industrial & Engineering Chemistry Research, 39(3), 610-619.
<https://doi.org/10.1021/ie990533k>

³⁴ Qin, Y. H., Campen, A., Wiltowski, T., Feng, J., & Li, W. (2015). The influence of different chemical compositions in biomass on gasification tar formation. Biomass and Bioenergy, 83, 77-84.
<https://doi.org/10.1016/j.biombioe.2015.09.001>

³⁵ Bailón Allegue, L., & Hinge, J. (2012). Biogas and bio-syngas upgrading. Danish Technological Institute.
https://www.teknologisk.dk/_/media/52679_Report-Biogas%20and%20syngas%20upgrading.pdf

³⁶ Krishnan, G. N., Canizales, A., Gupta, R., & Ayala, R. (1999). Development of disposable sorbents for chloride removal from high temperature coal-derived gases (Contract No. DE-AC21-93MC30005). U.S. Department of Energy.

³⁷ Ohtsuka, Y., Tsubouchi, N., Kikuchi, T., & Hashimoto, H. (2009). Recent progress in Japan on hot gas cleanup of hydrogen chloride, hydrogen sulfide and ammonia in coal-derived gas. Powder Technology, 190, 340-347.

³⁸ Bläsing, M., & Müller, M. (2013). Investigation of the effect of alkali metal sorbents on the release and capture of trace elements during combustion of straw. Combustion and Flame, 160(12), 3015-3020.
<https://doi.org/10.1016/j.combustflame.2013.08.005>

Gas turbine	n/a	<20	<50	<0.02	<1
Fischer-Tropsch 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

^a Units in ppmV; ^b Units in mg/Nm³.

1.2. INFLUENCE OF FEEDSTOCK & GASIFICATION CONDITIONS

The feedstock composition and operational gasification conditions have been identified as two of the most relevant parameters influencing the type and abundance of the impurities in the producer gas.

As mentioned previously, production of tar is influenced by several variables, including the gasifier type, gasification agent, pressure, residence time, and the presence of a catalyst. These factors have significant effects on both the quantity and composition of tar. With regard to the influence of biomass composition, there is no clear pattern regarding specific components in biomass contributing to tar formation, as shown in Figure 3.³⁹

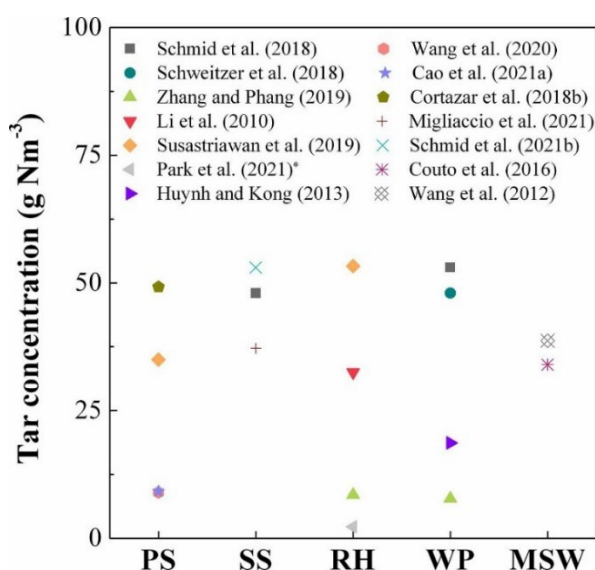


Figure 3: Tar concentration for various biomass feedstocks (PS: pine, SS: sewage sludge, RH: rice husk, WP: wood pellets, MSW: municipal solid waste).³⁹ * Result not given in dry basis.

Other factors, such as operating conditions and type of reactor, might have a greater influence on tar composition than biomass type. Due to ease of operation and economies of scale, fluidized-bed gasifiers with steam or air as a fluidizing medium are used in various gasification approaches. For steam gasification in a dual-fluidized circulating bed gasifier, differences in tar formation can be attributed to the tar cracking capabilities of the ash minerals present in some biomass sources, such as straw and sewage sludge.⁴⁰ For example, gravimetric tar yields from sewage sludge pellets have been reported higher (approximately 80 g/kg) when compared to those from lignocellulosic biomass (wood pellets approximately 20 g/kg) due to the aromatic structures present in sewage sludge.⁴¹ The operational

³⁹ Cortazar, M., Santamaria, L., Lopez, G., Alvarez, J., Zhang, L., Wang, R., Bi, X., & Olazar, M. (2023). A comprehensive review of primary strategies for tar removal in biomass gasification. *Energy Conversion and Management*, 276, 116496. <https://doi.org/10.1016/j.enconman.2022.116496>

⁴⁰ Schmid, J. C., Wolfesberger, U., Koppatz, S., Pfeifer, C., & Hofbauer, H. (2012). Variation of feedstock in a dual fluidized bed steam gasifier—influence on product gas, tar content, and composition. *Environmental Progress & Sustainable Energy*, 31, 205-215. <https://doi.org/10.1002/ep.11607>

⁴¹ Schweitzer, D., Gredinger, A., Schmid, M., Waizmann, G., Beirow, M., Spörl, R., & Scheffknecht, G. (2018). Steam gasification of wood pellets, sewage sludge and manure: Gasification performance and concentration of impurities. *Biomass and Bioenergy*, 111, 308-319. <https://doi.org/10.1016/j.biombioe.2017.02.002>

gasification temperature, type of bed material, and type of fluidizing medium have a significant effect on tar formation. When comparing tar yields from the fluidized-bed gasification of two biomass types, it was observed that above 800 °C, tar yields from cornstalks were higher than those from sawdust gasification, as shown in Figure 4.⁴²

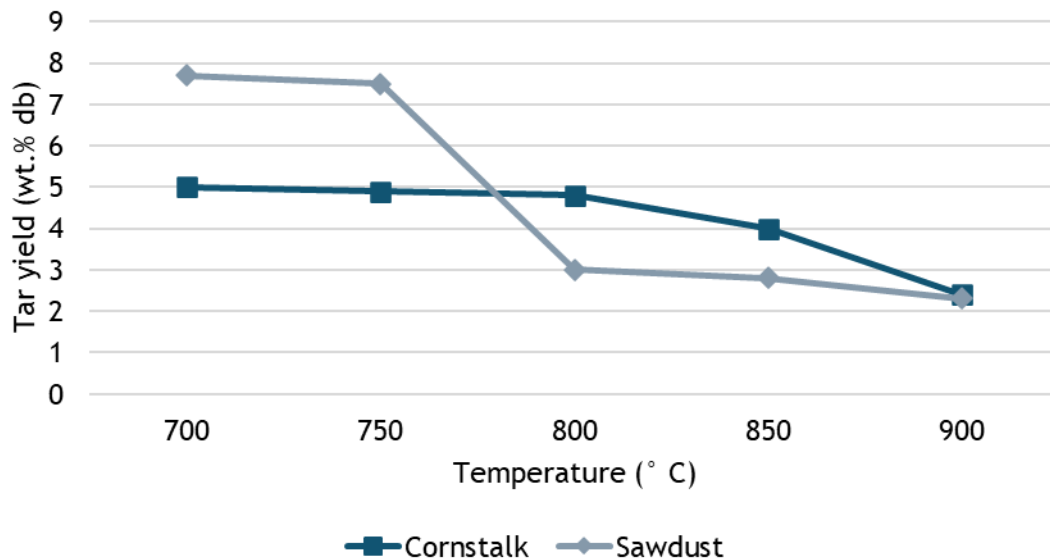


Figure 4: Tar yield of sawdust and cornstalks in a spouted-fluidized bed (adapted from YuHong Qin et al., 2015)

Table 8 shows tar abundance from the gasification of various types of biomass, at different temperatures and using air or steam as gasifying agents.

Table 8: Impurity Concentration Ranges for Biomass Gasification Producer Gases: Tars⁴³

Biomass	Bed Material	Gas Agent	Temp. °C	mg/Nm ³
Park wood	Inert (unspecified)	Air	861	245
Demolition wood		Air	847	383
Willow		Air	827	510
Chipboard		Air	843	658
Sawdust	Inert (silica)	Air	815	400
Sawdust		Air	700	15,200
Softwood	Active (olivine/limestone)	Steam	780	530
	Active (feldspar/limestone)			580
	Inert (quartz)			5,210
Forestry wood chips	Inert (unspecified)	Steam	850	19,000
Forestry softwood			847	9,000
Waste wood			847	25,000
Bark pellets			846	9,000

⁴² Qin, Y., Campen, A., Wiltowski, T., Feng, J., & Li, W. (2015). The influence of different chemical compositions in biomass on gasification tar formation. *Biomass and Bioenergy*, 83, 77-84. <https://doi.org/10.1016/j.biombioe.2015.09.001>

⁴³ de Oliveira, D. C., Sansaniwal, S. K., Kulkarni, M., & Vakharia, V. (2023). Gas cleaning systems for integrating biomass gasification with Fischer-Tropsch synthesis - A review of impurity removal processes and their sequences. *Renewable and Sustainable Energy Reviews*, 172, 113047. <https://doi.org/10.1016/j.rser.2022.113047>

Biomass	Bed Material	Gas Agent	Temp. °C	mg/Nm ³
Almond shells	Active (olivine)	Steam	770	600
	Active (dolomite)			2,400
	Inert (sand)			43,000
Pinewood chips	Active (dolomite)	Air	820	1,900
			820	3,400
			800	7,900
Conifer sawdust	Active (magnesite)	Air	804	9,700
Bark			848	10,800
			847	15,400
Wood pellets	Active (limestone)	Steam	655	29,000
			651	31,000

The selection of gasifier type can have a major effect on the development of tar during the gasification procedure, as shown in Figure 5.⁴⁴ The tar content in entrained flow and circulating fluidized-bed reactors is often found to be rather low, typically falling within the range of 0 to 5 g/Nm³ and 0 to 10 g/Nm³, respectively. The gasifiers employ gas streams with high velocity to facilitate the transportation and gasification of the feedstock particles. The quick reactions facilitated by the intensive mixing and short residence time in entrained-flow gasifiers contribute to the efficient conversion of tars into lighter gases, hence minimising the overall tar generation. Spouted beds and updraft fixed beds tend to produce far higher amounts of tar, with levels reaching up to 140 g/Nm³. Fixed-bed gasifiers are designed to function using a stationary or moving bed of feedstock, typically operating at comparatively lower temperatures. The production of tar in fixed-bed gasifiers is substantial as a result of restricted mixing and a longer residence time. These circumstances promote subsequent reactions that result in the production of tars.

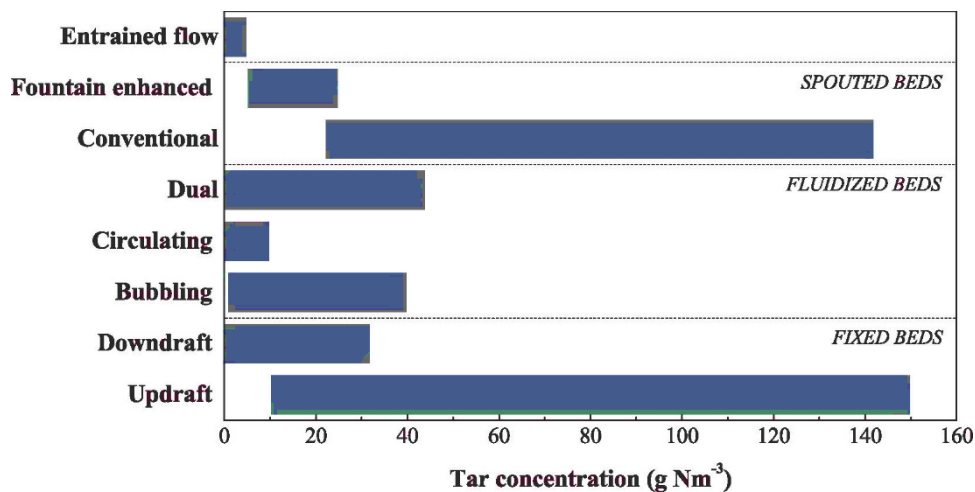


Figure 5: Tar yield of sawdust and cornstalks in the spouted-fluidized bed

Fountain-enhanced spouted beds, dual-fluidized beds, and bubbling fluidized beds have been seen to generate smaller levels of tar, with a maximum threshold of 50 g/Nm³. Fluidized-bed gasifiers are designed to suspend the feedstock within an upward-flowing gas stream, inducing a fluid-like behaviour. The dynamic and homogenised conditions present in fluidized-bed gasifiers have been observed to contribute to a decrease in tar production in comparison to fixed-bed gasifiers. The elevated temperature

⁴⁴ Cortazar, M., Santamaria, L., Lopez, G., Alvarez, J., Zhang, L., Wang, R., Bi, X., & Olazar, M. (2023). A comprehensive review of primary strategies for tar removal in biomass gasification. *Energy Conversion and Management*, 276, 116496. <https://doi.org/10.1016/j.enconman.2022.116496>

within fluidized-bed gasifiers can also potentially enhance the process of tar cracking and facilitate its conversion into lighter gases.

The downstream use is dependent upon the aggregate quantity of tar included in the producer gas. Applications focused on the production of motor fuels, such as H₂ production, Fischer-Tropsch synthesis, and methanol and natural gas synthesis, have stringent requirements for tar levels, typically below 1 mg/Nm³. In contrast, power generation equipment, such as gas turbines, gas engines, fuel cells, or boilers, have more lenient limits, ranging from less than 1 to 100 mg/Nm³. In general, tar concentrations in the conventional gasification processes result in producer gases with tar concentrations that are above the permitted threshold for the applications specified. Therefore, it is necessary to remove or convert tar to prevent the occurrence of excessive maintenance requirements during the upgrading procedures. Additionally, proper training of operators on optimizing the process temperature and residence time can help in mitigating the tar-related issues.

1.3. SYNGAS CLEANUP TECHNOLOGIES

The process of syngas cleanup refers to the removal of impurities such as tars, sulphur, nitrogen, and trace metals from syngas before it is further processed for various purposes. Syngas cleanup is typically a comprehensive and interconnected process involving multiple systems, with the selection of these systems being influenced by the factors outlined below:

2. Various categories of contaminants present in the syngas composition are of interest.
3. The extent of contaminant presence within the syngas is a matter of concern.
4. The upper limit of contaminant concentration is crucial for safeguarding the catalysts employed in syngas refinement.
5. The threshold concentration of certain contaminants in the resultant fuel is of paramount importance.
6. There are current technologies used at a commercial level, capable of producing contaminant-free syngas.

The high initial and ongoing cost of syngas purification arises from the variable mix of biomass and waste feedstocks. In general, an integrated multisystem approach to syngas cleaning aims to reduce capital and operational costs while optimizing thermal and carbon conversion efficiencies. The process of syngas cleanup can be categorized into two main classifications—primary and secondary measures—as shown in Figure 6.⁴⁵

⁴⁵ de Oliveira, D. C., Lora, E. E. S., Venturini, O. J., Maya, D. M. Y., & Garcia-Pérez, M. (2023). Gas cleaning systems for integrating biomass gasification with Fischer-Tropsch synthesis - A review of impurity removal processes and their sequences. *Renewable and Sustainable Energy Reviews*, 172, Article 113047. <https://doi.org/10.1016/j.rser.2022.113047>

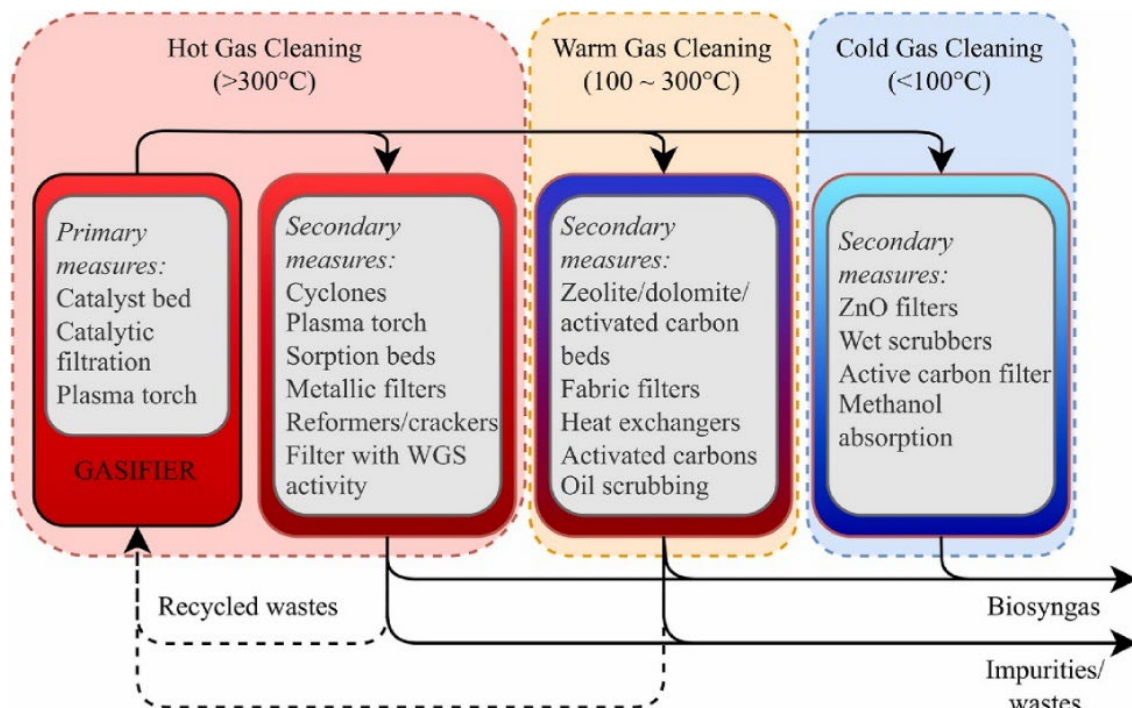


Figure 6: Primary and secondary measure examples in hot, warm, and cold gas cleaning processes⁴⁵

The primary measures encompass several systems that are incorporated within the gasifier with the objective of mitigating and minimizing the generation of pollutants throughout the process of gasification. Secondary measures refer to technological installations that are positioned downstream of the gasifier. The classification of technologies employed in this context encompasses physical and chemical systems, which are chosen according to the predominant types of contaminants found and the intended application of the syngas. An overview of impurity removal processes and their sequence is shown in Figure 7 for Fischer-Tropsch synthesis.⁴⁶ It also summarizes various information from feedstock synthesis to the gas cleaning step. The green line represents the simplest route in which tars are removed by cooling the produced gas to tar dew point, whereas the yellow line presents the alternate route in which tar is reformed to break it into smaller components for Fischer-Tropsch feed. Most of the cleanup process mentioned in this review is from primary and secondary methods used for producing clean syngas from the gasification process.

⁴⁶ de Oliveira, D. C., Lora, E. E. S., Venturini, O. J., Maya, D. M. Y., & Garcia-Pérez, M. (2023). Gas cleaning systems for integrating biomass gasification with Fischer-Tropsch synthesis - A review of impurity removal processes and their sequences. *Renewable and Sustainable Energy Reviews*, 172, Article 113047. <https://doi.org/10.1016/j.rser.2022.113047>

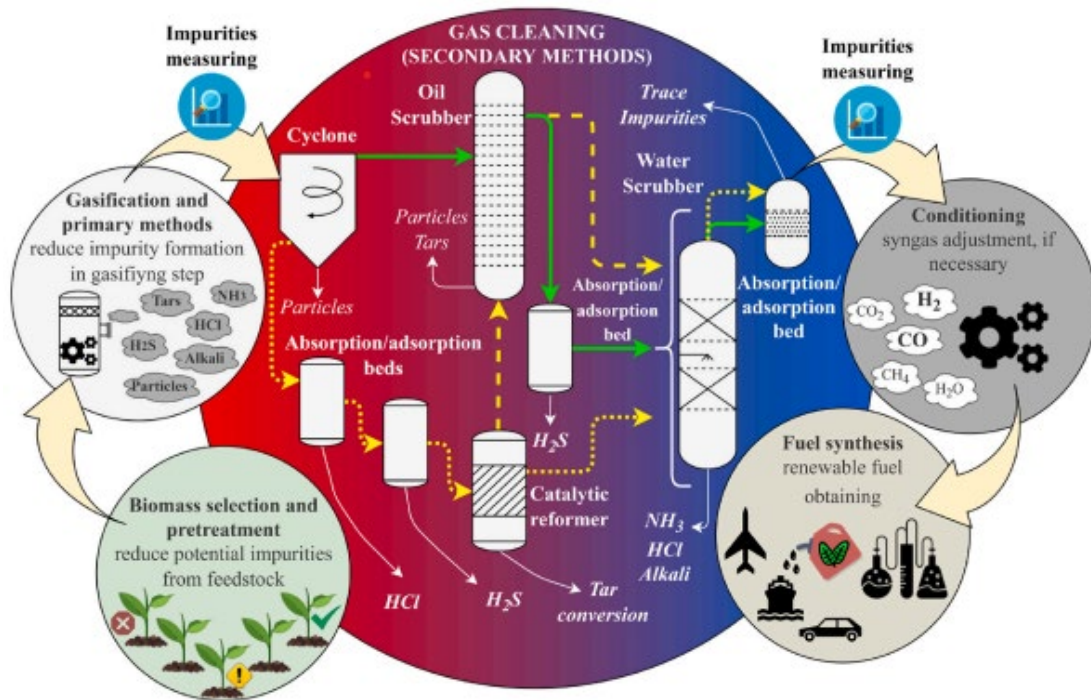


Figure 7: Biomass-to-liquid route representation, with emphasis on the gas cleaning sequence. The continuous green arrow represents the simplest route⁴⁶. The tar reforming route is marked with a yellow dotted line (the dashed one is an alternative path).

1.4. CASE STUDY

1.4.1. Kew Technology

Kew Technology is a sustainable energy solutions company working on the conversion of low-grade biomass and waste at commercial scale. Kew Technology is located in the West Midlands region in the United Kingdom and produces low-carbon, hydrogen-rich gases and fuels to be used across different energy sectors.

Their gasification technology operates at high pressure (8 bar), allowing them to achieve modularity, high-quality syngas output, and good product and carbon capture economics. They are currently expanding their approach into a solution using bioenergy with carbon capture and storage, as well as hydrogen greenhouse gas removal. A simplified diagram is shown in Figure 8.

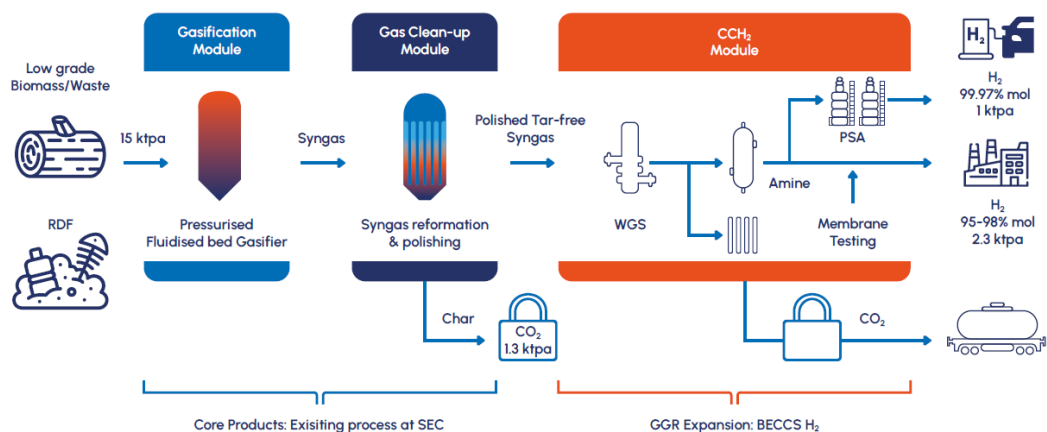


Figure 8: Kew Technology: bioenergy with carbon capture and storage (BECCS) and hydrogen greenhouse gas removal (H₂ GGR)

Their gas cleaning system removes all inorganic contaminants including sulphur compounds. As a result, the output stream is a tar-free syngas. Kew has patented this polishing syngas unit technology with some second-stage reforming units that remove tars from syngas and rearrange molecules to have a stable syngas composition independently from input feedstock. Their single module features a module capacity of 8.6 MW feedstock, 6.2 MW clean syngas, and 72 % cold gas efficiency.

2. Status on Producer Gas Cleaning Overview

Gas cleaning in biomass gasification is a critical process aimed at removing impurities from the syngas produced during biomass gasification. These impurities typically include tar, particulate matter, sulphur compounds, and alkali metals. The efficiency and effectiveness of gas cleaning directly impact the quality of the syngas, which in turn affects downstream processes such as power generation, chemical production, or biofuel synthesis. This chapter describes the state of the art on gas cleaning.

2.1. PARTICULATE MATTER AND METALS REMOVAL

2.1.1. Particulates Removal

Larger particulate can be recovered utilizing inertia-driven separation devices such as cyclones, impact devices, or settling chambers. This coarse material can be recycled back to the gasifier for further conversion if it contains significant carbon. While inertial separation devices are suitable for large particulates ($>10\mu$), a significant amount of fine ash and carbon will exit the gasification process and not be captured in cyclones (etc.). Additional particulate control can be accomplished using water scrubbing to capture the particles in liquid droplets, allowing the particulate to be recovered as a sludge. This sludge is typically fed into settling ponds, with the settled solids recovered for disposal after further concentrating by either filtration or thermal drying. The particulate can then be landfilled, utilized as a secondary fuel (if enough residual energy justifies the extra capital cost), or reutilized for secondary product use such as cement production and road fill.

One option to capture essentially all fine particulates is the use of commercial candle filter systems designed for operation at moderate temperature and pressure. These devices—sometimes called hot gas filters—utilize rigid filters made from high-temperature metallic alloys such as sintered stainless steel, Inconel, Hastelloy, or iron aluminide. Candle filter systems based on ceramic candle materials such as SiC and alumina-silicate refractory fibre are also available. These devices typically operate about 30°C above the dew point of tar or steam, which allows the fine particulate to be recovered in a dry state and prevents ash from sticking to the filter surface. Several commercial vendors offer complete candle filtration systems, including Pall Advanced Separations, Porvair Filtration Group, Mott Corporation, and Saifilter. Other vendors (including Unifrax and Tenmat) supply individual filter elements compatible with most commercial systems. Because of the relatively high pressure drop through candle filters, they are only suitable for pressurized gasification systems. Atmospheric or subatmospheric gasifiers can instead use high-temperature bag filters that cause less pressure drop but are less effective at trapping fine particulate.

For either option, the filter media will accumulate fine particulate matter as a dust cake while syngas is flowing through the filter. Candle or bag filters must be periodically backpulsed by sending a burst of high-pressure gas to the filter outlet, causing gas to briefly flow backward through the filter to knock the dust cake loose. These solids then fall into a cone and are drained and recovered. While backpulsing does not affect the performance of candle filters, bag filters lose some effectiveness immediately after each backpulse because the thickening dust cake provides extra filtration. This can preclude the use of bag filter systems when downstream process reactors or other systems cannot tolerate any particulate.

Figure 9 depicts a commercial candle filter system. Most candle filters systems are designed to maintain continuous syngas flow through the filter system by backpulsing only certain banks of filter elements at a time, allowing the other filters to continue operating. Depending on the dust loading and filter ash properties such as particle size, amount of carbon, and aerodynamic drag, the filter system must maintain a low gas velocity across the face of the filters (generally between 1 and 4 cm/s). Filter elements with longer lengths increase the surface per filter element to allow higher flow and higher dust loading. For large gasification systems, multiple candle filter pressure vessels are required to provide enough filter surface area, with the total syngas flows being split between the separate vessels.

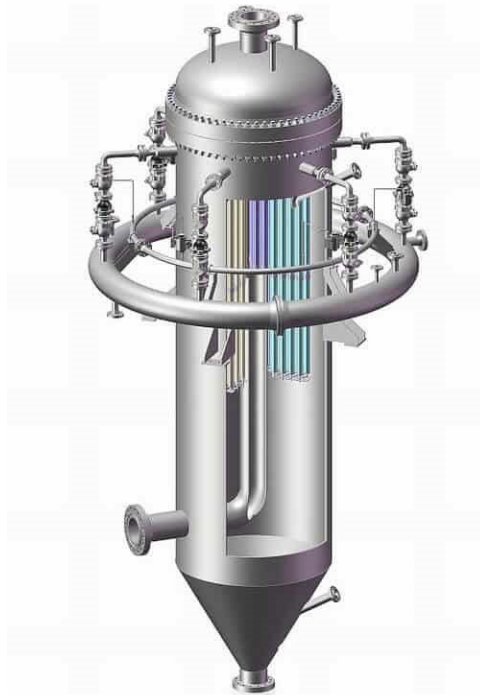


Figure 9: Saifilter hot gas candle filter system⁴⁷

2.1.2. Metals Removal

Alkali and alkaline earth metals, principally potassium, sodium, and calcium, are present in biomass. The concentration of total inorganics can range from 0.5 to 15 wt % depending on feedstock. Alkali and alkaline earth metals in biomass are typically in the range 0.2-1 % by weight.⁴⁸ A typical metals profile for a sample of white oak from the United States is shown in Table 9.

These metals, which are naturally occurring in biomass, can be highly problematic if they are present in biomass-derived syngas due to a number of issues associated with either the gasifier itself or unit operations downstream of the gasifier. Some of these compounds may form low-melting eutectics in the gasifier, hampering operations for fluid beds. Many are volatile and will escape the gasifier with the syngas, presenting issues with heat exchangers, compressors, and catalyst beds downstream of the gasifier. If these metals persist and are not removed, fouling of systems can take place, reducing operating efficiency and increasing maintenance costs. Critically, permanent poisoning of catalysts can take place as some of these materials will plate out on catalyst surfaces and are not readily removed by normal regeneration protocols (e.g., coke burning).

Table 9: Metals Found in Ash From White Oak⁴⁹

Metal	Wt % in Ash
Aluminium	0.91
Calcium	42.4
Chromium	Below detection limit

⁴⁷ SAI Filter. (n.d.). Hot gas filter system | High temperature gas filtration. Retrieved August 2023, from <https://www.saifilter.com/products/hot-gas-industry-filter/>

⁴⁸ Shafizadeh, F. (1968). Pyrolysis and combustion of cellulosic materials. *Advances in Carbohydrate Chemistry*, 23, 419-474.

⁴⁹ Baldwin, R. M., & Feik, C. J. (2013). Bio-oil stabilization and upgrading by hot gas filtration. *Energy & Fuels*, 27(6), 3224-3238. <https://doi.org/10.1021/ef400177t>

Metal	Wt % in Ash
Iron	0.71
Magnesium	2.02
Manganese	Below detection limit
Molybdenum	Below detection limit
Nickel	Below detection limit
Phosphorus	2.62
Potassium	18.9
Silicon	3.82
Sodium	0.43
Zinc	Below detection limit

2.1.2.1. Halogen Removal

Halogens in the form of hydrogen halides are particularly problematic if found in syngas due to the potential for corrosion of downstream unit operations (e.g., syngas compressor). HCl and other hydrogen halides are commonly removed by wet scrubbing, usually through a caustic solution (NaOH in water) or, alternatively, simply water.⁵⁰ In addition, caustic water can remove other contaminants such as COS and CO₂.

Gas cooling can induce the condensation of volatile metals—particularly alkali metals—if syngas temperatures are reduced to below 600 °C.⁵¹ This approach may be relatively ineffective for deep gas cleaning, as some metals will remain in the vapor phase. Most trace metals, like alkali metals, are sufficiently soluble in water and can consequently be co-absorbed in water during wet scrubbing of tar and ammonia.

2.1.2.2. Metals Removal by Hot Gas Cleanup

Metals in syngas, as well as particulates such as char and ash particles, can be effectively removed from hot syngas by application of hot gas filters as described above. This technology has been shown to be effective in reducing the metal content in syngas, as well as bio-oil produced by pyrolysis of woody biomass to levels that provide an almost zero-ash product. Table 10 presents results of hot gas filtration for a laboratory-scale hot gas filter system for cleanup of biomass pyrolysis vapours. Hot gas filtration also can be combined with catalytic cracking and reforming of tars in syngas by coating the external surface or impregnating the candle filters with a suitable catalytic material. Other embodiments of this technology involve use of the filter inside the gasifier vessel itself rather than in a separate vessel downstream from the gasifier.

Table 11: Hot Gas Filtration of Bio-Oil Vapours at 450 °C⁵²

Metal	Raw Oil ppm	HGF Oil ppm
Aluminium	4	<2
Calcium	19	<10
Chromium	<1	<1
Iron	<5	<5

⁵⁰ Allegue, L. B., & Hinge, J. (2012). Biogas and bio-syngas upgrading. Danish Technological Institute

⁵¹ Salo, K., & Mojtahedi, W. (1998). Fate of alkali and trace metals in biomass gasification. *Biomass and Bioenergy*, 15(3), 263-267

⁵² Baldwin, R. M., & Feik, C. J. (2013). Bio-oil stabilization and upgrading by hot gas filtration. *Energy & Fuels*, 27(6), 3224-3238. <https://doi.org/10.1021/ef400177t>

Metal	Raw Oil ppm	HGF Oil ppm
Magnesium	<1	<1
Manganese	<1	<1
Molybdenum	<1	<1
Nickel	4	<1
Phosphorus	<5	<1
Potassium	40	<5
Silicon	<10	<10
Sodium	37	<5
Zinc	<1	<1

2.2. TAR REMOVAL

Tar represents one of the greatest ongoing challenges facing biomass gasification. Tars can be defined as condensable organic compounds that are generally in the range of C₆ or higher and are present as vapor-phase compounds in syngas. Broadly speaking, tar production from a gasifier is most strongly influenced by the amount of volatile matter in the fuel and by the reaction temperature. Much gasification knowledge is derived from years of experience with coal-fed systems; however, biomass by its nature contains more volatile matter than coal, which exacerbates the tar mitigation problem. Biomass is also generally more fibrous than coal, which can make it more challenging to pulverize into very small regular particles. Pulverized fuel can be quickly mixed with oxidant to react at the high temperatures (approximately 1,000°C or higher) that favour tar cracking, while larger particles take longer to react and are better suited for lower-temperature operation. Biomass also tends to contain more moisture and have less heating value than coal, which further works to reduce maximum gasifier temperature. Because biomass is rich in volatile matter and more challenging to gasify at high temperature, it is more prone to tar formation during gasification, especially in systems that are being adapted from coal-based applications.

There are several approaches to handling tar in syngas that can be broadly grouped into two categories:

1. Upfront efforts in feed conditioning and gasifier design to mitigate tar formation.
2. Downstream syngas processing to minimize tars in the syngas.

On the front end, biomass can be dried and torrefied into a coal-like material that has reduced volatile matter and can be more readily gasified at the high temperatures that favour tar cracking. During gasification, if biomass is fed into a fluidized-bed gasifier, bed additives can be used, which act as catalysts to encourage tar cracking at reduced temperatures. At the gasifier outlet, tar can be thermally cracked by increasing the syngas temperature, such as by injecting oxygen to burn a portion of the syngas or catalytically reformed to produce additional syngas from the tars. Further downstream, tar can be scrubbed from the syngas or otherwise captured. Each approach has its advantages and limitations, as outlined below.

2.2.1. Gasifier Design and Feed Conditioning

2.2.1.1. Torrefaction

Torrefaction involves heating biomass to moderate temperature (approximately 300°C or lower) in a low-oxygen atmosphere to avoid combustion. This drives off moisture and low-molecular-weight volatile matter while causing other components to partially decompose and polymerize to form an energy-dense carbonaceous material. The final torrefied product is more similar to coal in heating value, carbon content, and grindability than raw biomass, allowing torrefied biomass to potentially act as a drop-in replacement for coal in existing gasifier designs that are optimized for processing coal. A number of companies have pursued commercial torrefaction over the years, including Thermya out of France and NextFuel out of Scandinavia.

Despite several attempts at commercialization and the obvious benefit of making a coal-like product from raw biomass, most efforts at large-scale commercialization of torrefaction have so far failed to materialize. One of the key issues with torrefaction is that the gaseous byproducts are reactive and can form tars that condense and coat downstream equipment as they cool. This issue effectively pushes the tar removal problem upstream from the gasifier to the torrefaction unit. Aside from tar formation, another concern with torrefaction is that torrefied biomass must be cooled to below its autoignition temperature before it is exposed to air. Heat management becomes a challenge at large scale because of the high throughput of biomass. Adding torrefaction at the gasifier site can result in improved operability at the cost of greater complexity and higher capital expenses.

2.2.1.2. Gasifier Design

Tar formation is heavily influenced by temperature, and gasifiers that operate at sufficiently high temperatures tend to produce reduced amounts of tar. These gasifiers often operate hot enough that ash in the feed will melt to form liquid slag. This limits gasifier designs because options such as fluidized beds require that solid particles be able to move freely, and slag will cause particles to stick together and defluidize. The feed also must have enough heat content to sustain extremely high temperatures and must be able to be pulverized to very fine particle sizes; both factors may require torrefaction of raw biomass feedstock.

Common slagging gasifier designs include the entrained-flow gasifier, in which finely pulverized solids are co-fed with air, oxygen, and/or steam. The high surface area of the pulverized fuel allows it to rapidly convert with the mixed oxidant to generate high temperatures and fully convert tars and other components into gaseous products such as CO₂, CO, and H₂, with very low levels of any light hydrocarbons. The high temperatures and slagging conditions result in reduced thermal efficiency (because more fuel must be oxidized to provide heat) and high wear on system components exposed to slag. Some designs attempt to reduce wear on manufactured components by cooling the gasifier shell, causing a layer of slag to harden over the refractory and offer some protection from the corrosive gasifier environment. There is extensive experience using entrained-flow gasifiers for coal conversion, with major past and current commercial technology vendors including General Electric, Shell (both now licensed from Air Products), and various others.⁵³

2.2.1.3. Plasma Reforming

At the extreme high temperature range, plasma gasification uses a plasma torch to achieve extremely high temperatures (approximately 6,000 °C) of the reactor, which can convert carbonaceous feedstocks almost entirely into slag and syngas. The plasma torch requires an electric arc, so for power generation applications, some portion of the power generated by the plant is consumed to power the plasma torch. A common application of plasma gasification has been for waste processing such as medical waste. Because of the small scale of waste processing facilities and the high energy demand for plasma generation and other process needs, plasma gasification facilities can consume more power than they generate, and the incentive for plasma gasification may be driven by emissions reductions more so than by needs for power or syngas production. Commercial plasma gasification units were installed in Japan by Hitachi during the late 1990s and early 2000s, primarily for handling municipal solid waste, as the extremely high temperatures were effective at breaking down dioxins and other hazardous pollutants. The largest of these units were decommissioned as of 2013.⁵⁴ A small-scale plasma gasifier installed in 2013 was reportedly still running as a means of waste disposal on a U.S. aircraft carrier as of October 2022.⁵⁵ Two large (50-MW) municipal solid waste direct plasma gasification projects being constructed by Air Products

⁵³ National Energy Technology Laboratory. (n.d.). Entrained flow gasifiers. Retrieved October 2023, from <https://netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/entrainedflow>

⁵⁴ National Energy Technology Laboratory. (n.d.). Plasma gasification. Retrieved October 2023, from <https://netl.doe.gov/research/Coal/energy-systems/gasification/gasifipedia/westinghouse>

⁵⁵ Bath, A. (2022, November 28). [Article in Stars and Stripes]

at a Teesside facility in the UK were abandoned in 2016 due to significant operational difficulties.⁵⁶

Plasma reformers can also be used as a second-stage gasifier to crack the tars exiting a lower-temperature first-stage gasifier and produce additional syngas. Pilot-scale test systems have reported 90 % to 95 % tar conversion using plasma systems operating on the outlet of updraft fixed-bed gasifiers.⁵⁷ Somewhat better tar conversion has been observed on the outlet of fluid-bed gasifiers,⁵⁸ presumably due to the lower inlet tar concentration from fluidized-bed systems. Deep cleaning of syngas tars may still require some additional tar conversion or removal process. Small-scale processes may show good performance that rapidly falls off when the process is scaled up, mainly because of difficulties in maintaining a uniform plasma over the entire reaction flow path with larger equipment. As such, early designs may show promise that is difficult to implement, and careful design work during scale-up is required to eliminate plasma nonuniformities in the syngas flow profile. OxEon Energy LLC (formerly Ceramatec Inc.), AlterNRG, Heartland Technologies, and Omni Technologies all offer plasma technologies that have been tested in larger-scale systems. Omni Technologies' 200-ton/day commercial municipal solid waste plant design claims almost complete tar conversion at temperatures 300 °C to 400 °C lower than what would be required without the use of plasma⁵⁹ and has reportedly been selected for use in municipal solid waste conversion plants slated to be operational within the next several years.

2.2.1.4. In Situ Tar Reduction

For fluidized-bed gasifiers, reaction temperature is limited by ash melting temperature, but the choice of bed material can help to reduce tar formation by acting as a catalyst to crack tars at relatively low temperatures. Common bed materials known to have some moderate tar cracking ability include low-cost solids such as calcined limestone, dolomite, and olivine.⁶⁰ One issue with use of in situ tar reduction is that the catalyst can coke or be lost over time (due to attrition) and will need to be replenished to maintain tar cracking performance. This need to continually add and replace bed material limits options to those compounds that are inexpensive, even when research has shown that more costly materials would be more effective at tar cracking. Another limitation with the in-situ approach is it can only crack a portion of the tar, and further treatment is normally required for deep tar removal. Higher temperatures may encourage additional tar cracking, but some of the high-alkali materials found in biomass act as fluxing agents to melt bed materials, which limits the temperature at which a fluidized bed can operate. As such, in situ tar reduction can be viewed as a component of tar reduction but not as a full deep-cleaning solution.

2.2.1.5. Syngas Processing

If tars are not prevented from forming through gasifier design and/or in situ conversion and feed conditioning, they must be reduced after formation through syngas processing. There are several approaches to syngas processing for tar reduction, including thermal cracking, catalytic tar reforming, partial oxidation, scrubbing, and absorption.

2.2.1.6. Ex Situ Thermal Cracking and Catalytic Tar Reforming

Thermal cracking and reforming is the conversion of the tar in an oxygen-free environment, often at

⁵⁶ Air Products to ditch plasma gasification waste to energy plants. (2016, April 5). Waste Management World. <https://waste-management-world.com/artikel/air-products-to-ditch-plasma-gasification-waste-to-energy-plants-in-teesside/>

⁵⁷ Soedarsono, H. P., Faizal, F., Panatarani, C., & Joni, I. M. (2022). Carbon functionalized material derived from byproduct of plasma tar-cracking unit on biomass gasifier collected using standard impinger method. *Processes*, 10(9), 1733. <https://doi.org/10.3390/pr10091733>

⁵⁸ Materazzi, M., Lettieri, P., Mazzei, L., Taylor, R., & Chapman, C. (2015). Reforming of tars and organic sulphur compounds in a plasma-assisted process for waste gasification. *Fuel Processing Technology*, 137, 259-268. <https://doi.org/10.1016/j.fuproc.2015.03.007>

⁵⁹ Omni Conversion Technologies Inc. (2023). Omni200™ gasification & plasma refining system (GPRS™). <https://www.omnict.com/wp-content/uploads/2023/08/OMNI-Process-Description-TMP-1202.pdf>

⁶⁰ Gómez-Barea, A., Ollero, P., & Leckner, B. (2013). Optimization of char and tar conversion in fluidized bed biomass gasifiers. *Fuel*, 103, 42-52. <https://doi.org/10.1016/j.fuel.2011.04.042>

temperatures greater than 900°C. Catalytic tar reforming improves tar reduction, generates significant additional syngas from the tars (thus improving the overall carbon efficiency of the process), and allows similar performance and reduced temperatures as compared to noncatalytic thermal cracking, but catalysts can be prone to deactivation. Nickel-based tar cracking catalysts initially show good performance, but most seem to suffer from significant catalyst deactivation due to impurity poisoning and carbon deposition in the catalyst pores during the tar reforming process. The National Renewable Energy Laboratory developed a catalyst that was tested both in a fluidized bed and a coated monolith structure that is less prone to deactivation by syngas impurities. Experimental and proprietary rhodium-based clover-leaf-shaped catalyst pellets developed by Johnson Matthey called JMR3 has also been successfully tested. Neither the National Renewable Energy Laboratory’s nor Johnson Matthey’s catalysts are currently commercially available. Very recently, Frontline BioEnergy has reported development of its ‘TarFreeGas’ technology using a catalytic gas converter.⁶¹ Further demonstration is required before the long-term performance of novel tar reforming catalysts can be fairly assessed.

2.2.1.7. Partial Oxidation

Partial oxidation offers the potential to almost completely remove tars without extra biomass processing or use of high-temperature gasifiers. In general, partial oxidation takes tar-laden syngas from a first-stage gasifier and reforms it in a second stage by burning oxygen, air, and/or steam, with or without supplementary fuel. Supplementary fuel could be natural gas or recycled syngas to avoid adding any fossil fuel to the process. Linde’s Hot Oxygen Burner technology is one commercial option (Figure 10) and is the process used by Sungas Renewables and Fulcrum Bioenergy’s Sierra Biofuels plant. Enerkem is also reportedly using a similar concept for tar reduction.

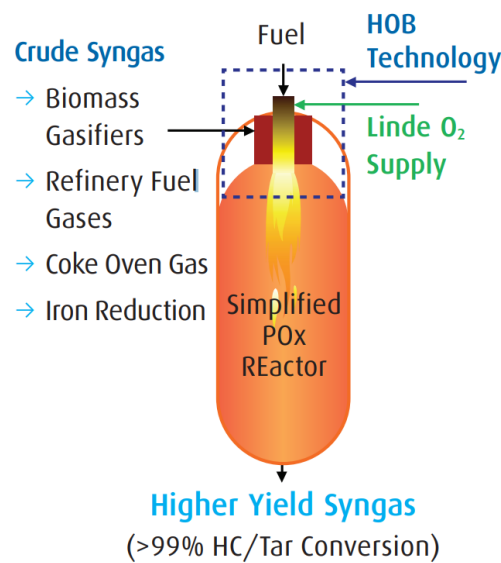


Figure 10: Linde Hot Oxygen Burner tar reforming process⁶²

2.2.1.8. Scrubbing

Scrubbing generally involves spraying water or an organic liquid into a column with syngas flowing upward. As the syngas cools, tar condenses from the vapor to the liquid phase, and the downward-flowing liquid droplets capture the tar. A common issue with this approach is in handling the condensed tars. Some tar components (e.g., naphthalene) form a solid phase that can coat surfaces, leading to plugging or reduced

⁶¹ Frontline BioEnergy. (2023, October 9). Frontline BioEnergy achieves breakthrough no-tar gasification technology. <https://frontlinebioenergy.com/news/frontline-bioenergy-achieves-breakthrough-no-tar-gasification-technology/>

⁶² Linde. (2020). Syngas reforming using hot oxygen burner technology (P-40-4561). https://assets.linde.com/-/media/global/usa/linde-us/literature/energy-decarbonization/p-40-4561_syngas-reforming-using-hot-oxygen-burner_linde-final---x.pdf

heat transfer. Recovered tars may also contain potentially hazardous materials that require further processing or hazardous waste disposal.

ECN has developed an oil-based tar scrubbing system for the removal of tars from syngas (Figure 11). This system operates below the tar dew point but above the moisture condensation temperature, so little liquid water is removed as part of the process. This system employs a multistage scrubber that condenses the heavier tars (plus particulate if no upstream filter is utilized) in an initial packed column collector in which condensed heavy tar and particulate are removed in the circulating oil and wet electrostatic precipitator. All the particulate, tar, and unrecovered residual oil recovered in the first stage are recycled to the gasifier for further conversion.

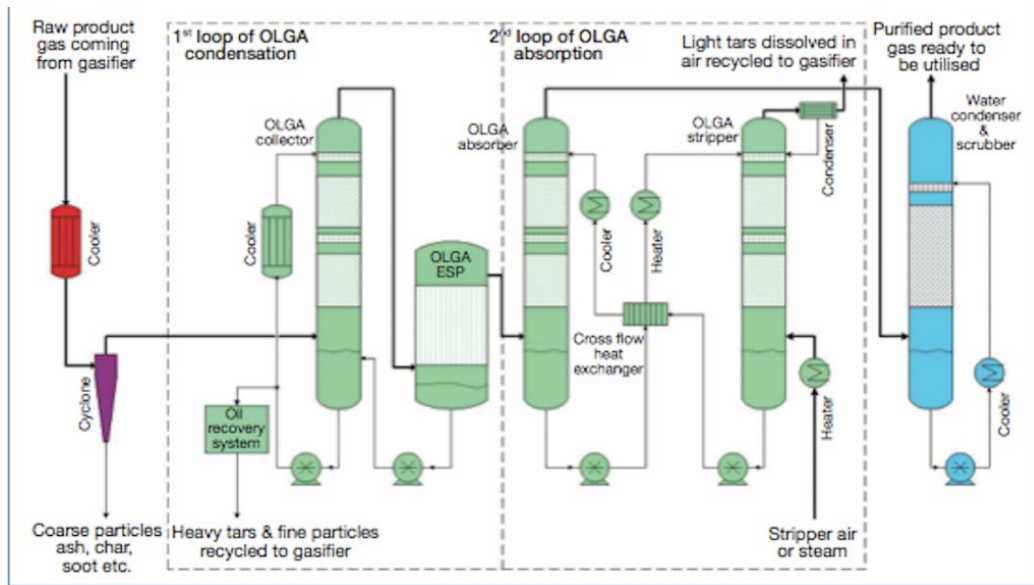


Figure 11: Schematic of OLGA tar removal system⁶³

The lighter tars (especially the phenols and naphthalenes) pass into a second absorber column in which the light tars are absorbed in the oil and then sent to an attached stripper column to be stripped with either air or steam to prevent the oil from becoming saturated with the light tars. The stripped light tars are returned to the gasifier in either the fluidization air or steam to be consumed. Approximately 25-50 % of the lightest aromatics such as benzene and toluene are removed by the OLGA process, while light alkanes are not removed. The OLGA system product gas typically passes to a water scrubber where ammonia and chlorides are removed. The OLGA system has been demonstrated up to a 4-MW_{th} scale with projected commercial systems up to 50 MWe. Since 2019, Synova has been the commercialization partner for the OLGA technology.

2.2.1.9. Activated Carbon Adsorption

While considered a more expensive option, several activated carbon manufacturers provide a product designed to adsorb light organics from gas-phase streams. Vendors include Calgon, Evoqua, and others. These granular activated carbon products are designed with a high surface area (generally >100 m²/g) to capture vapor-phase light organics from ambient-temperature syngas streams. These light hydrocarbons can be regenerated from the activated carbon by heating the bed, optionally under vacuum to favour devolatilization. Carbon vendors are able to help determine appropriate carbon type, regeneration conditions, and expected operating costs associated with a given gas stream. Characteristics of activated carbon are mainly determined by the parameters of the thermal regeneration process. At lower

⁶³ Staff report. (2015, January 1). MILENA and OLGA get together for high efficiency and low tar. Modern Power Systems. <https://www.modernpowersystems.com/features/featuremilena-and-olga-get-together-for-high-efficiency-and-low-tar-4815584/>

regeneration temperatures, the activated carbon adsorption capacity might not be restored, while if the regeneration conditions are too harsh, the adsorption properties and the original carbon structure are likely to be impaired, and loss of some of the sorbent may also occur. Makeup carbon used to replace that lost during regeneration, typically around 10-12 % of the total granular activated carbon mass, can represent 20-40 % of the total costs associated with granular activated carbon regeneration. Heavier multi-aromatic ring compounds are more difficult to thermally regenerate because of their lower vapor pressures at modest temperatures, resulting in more expensive direct carbon replacement rather than regeneration. Spent activated carbon that has been rendered non-regenerable must be sent off-site for thermal destruction as a hazardous waste stream.

2.3. SULPHUR REMOVAL

Sulphur in the form of H₂S is known to have a major impact on many catalysts, including those used for Fischer-Tropsch synthesis and fuel cells. As such, a great deal of work has gone into developing processes for removing sulphur from syngas, especially from historical work with coal. While many forms of biomass have lower sulphur content than high-sulphur coal, even small traces of sulphur (ppb) will still poison catalysts, and it is important to note what options exist when gasifying streams that may contain appreciable sulphur.

Gasification converts most sulphur in the feed into H₂S, with a small percentage being converted into COS, CS₂, and traces of organic sulfides such as methyl mercaptans (CH₃SH), ethyl mercaptan (CH₃CH₂SH), and heterocyclics like thiophenes (C₄H₄S). Generally, total sulphur levels need to be reduced to well below 1 ppm to achieve acceptable catalyst lifetimes for various processes utilizing syngas as a feed. Options for deep sulphur removal involve either the capture of the sulphur species by dissolution into various solvents or by the reaction of the sulphur species with solid sorbents.

2.3.1. Bed Additives

Some sulphur removal can be achieved by the reaction of the sulphur with alkaline species such as calcium or sodium inherent in the fuel ash, although this is considered to be fairly minimal depending on the ash content and chemistry of the particular feedstock. The addition of additives such as limestone or dolomite in a fluidized-bed gasifier has been demonstrated to enhance sulphur capture as sulfide by the reaction presented (Reaction 5). However, this reaction is reversible, and equilibrium constraints limit the amount of sulphur that can be captured because high concentrations of CO₂ and H₂O in syngas tend to drive the reverse reaction.



Air-blown fluid-bed gasification, where the partial pressures of the CO₂ and H₂O in the syngas are much lower, has demonstrated sulphur retentions up to 90 % at Ca/S molar ratios around 3. However, oxygen-blown fluid-bed gasifiers with much higher CO₂ and steam partial pressures tend to see the sulphur retention remain less than 40 % at the same molar ratio. In-bed additives are not typically utilized in fixed-bed gasifiers because of the poor mixing, while in entrained-flow slagging gasifiers, additives will form a slag and decompose, thereby limiting their effectiveness. Since most syngas conversion processes are likely to be oxygen-blown to achieve high concentrations of hydrogen and lower tar, the utilization of calcium-based additives is generally not recommended because of the higher cost associated with additives, handling, equipment, transportation, and additional ash handling and disposal costs.

2.3.2. Cold Gas Cleanup With Solvents

The most common commercially demonstrated sulphur removal technologies for syngas currently in use are solvent-based scrubbing systems. Figure 12 depicts the general types of solvents currently considered to be commercially available. Solvents include amines, dimethyl ethers of polyethylene glycol (DEPG) such as Selexol and AGR II, cold methanol such as the Rectisol process, and hot potassium carbonate (Benfield process). All these processes require that the syngas first be cooled to minimize moisture and tar in the syngas entering the solvent scrubbing column.

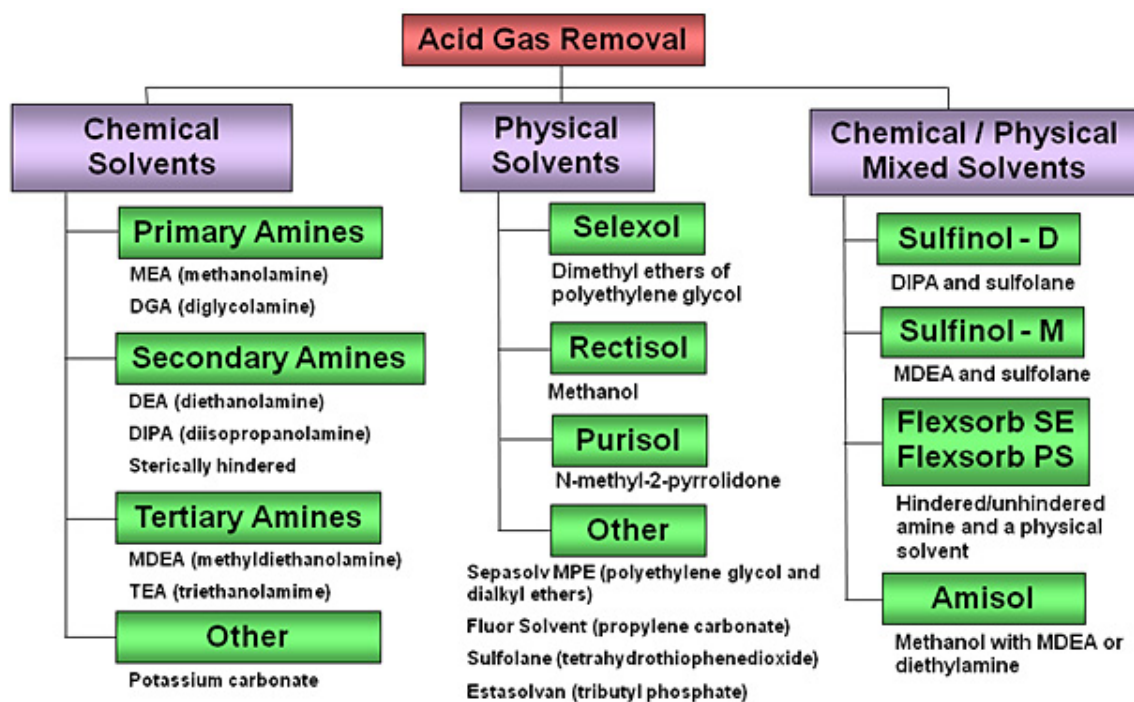


Figure 12: Solvent options for syngas cleaning⁶⁴

2.3.2.1. Amine Solvents

Amine-based solvents chemically react with H₂S and CO₂ to form ionic species that are soluble in water as presented below (Reactions 6 and 7). Amine-based solvents include diethanolamine, monoethanolamine, methyldiethanolamine, diisopropanolamine, and diglycolamine.



While amines are effective at capturing H₂S, they are not effective for other reduced forms of sulphur found in syngas. This can be overcome by using a COS hydrolysis reactor to convert COS to H₂S (Equation 8). COS hydrolysis reactors operate at about 175 °C-200 °C utilizing an alumina-based catalyst and can convert more than 99 % of COS to H₂S.



Figure 13 is a schematic depicting one possible configuration for an amine-based solvent system. In this configuration, lean solvent is sprayed into the top of an absorber tower with syngas in upflow. Solvent reacts with H₂S and CO₂ to form rich solvent that is then heated and passed to a stripper column. A steam reboiler at the bottom of the column provides heat to reverse the chemical reaction, freeing CO₂ and H₂S as acid gas and regenerating lean solvent. The lean solvent is then cooled and passed back to the absorber to complete the loop. An alternative configuration is to use a two-stage process to selectively recover H₂S separately from CO₂.

⁶⁴ National Energy Technology Laboratory. (n.d.). Acid gas removal (AGR). <https://netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/agr>

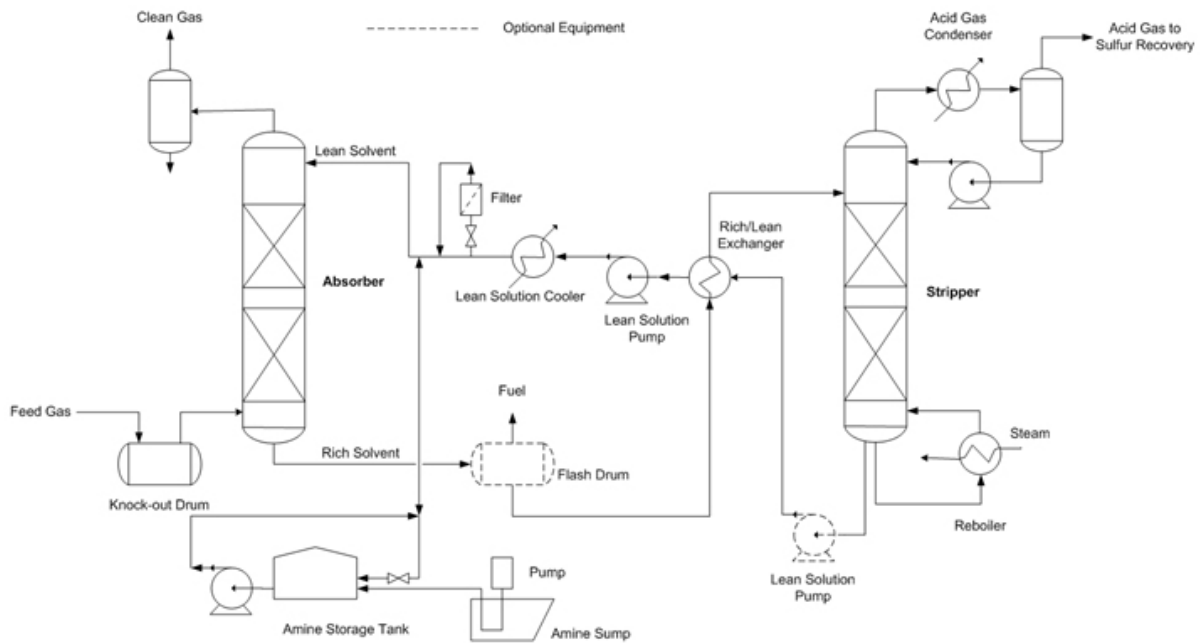


Figure 13: Generic amine scrubbing system⁶⁵

Amines require significant energy during the regeneration process to break chemical bonds. Steam is typically utilized as a heat source at temperatures between 130°C and 200°C. Vendors for these amine solvents include Shell, Dow Chemical, Mitsubishi Heavy Industries, and BASF, among many others. Current gasification plants utilizing this technology for sulphur removal include TECO, Wabash, and the Puertollano IGCC plants, along with numerous natural gas processing systems. Since these solvents have limited H₂S removal efficiencies down to near 10 ppm, additional sulphur polishing is required to achieve the deep sulphur cleaning required for most catalytic conversion processes.

2.3.2.2. Physical Solvents

Selexol: Selexol and similar processes use DEPG as a solvent, which has an affinity for H₂S and CO₂ due to the physical solubility of these acid gases at elevated pressures. The solubilities of acid gases, including COS and mercaptan, improve at lower temperatures (slightly chilled to between 5°C and 40°C) and elevated pressures (typically above 20 bar, preferably above 35 bar). Since these solvents are capable of removing various sulphur species, COS hydrolysis reactors are not required upstream of the solvent column. DEPG is also an excellent solvent for CO₂ capture, with two-stage systems available for the separate recovery of sulphur and CO₂ streams. Figure 14 depicts a generic two-stage DEPG process. Because acid gas does not chemically react with DEPG, regeneration requires much less energy than the amine solvents, and the bulk of the acid gases can be released with a simple flashing process. Suppliers of DEPG include Dow Chemical/UOP (licensed as Selexol/Selexol Max) and Breitag's Coastal Chemical Group (licensed as AGR II). Gasification facilities utilizing DEPG include the Chaparral/CVR Energy Coffeyville Gasification Plant in Kansas and Edwardsport IGCC in Indiana. The Energy & Environmental Research Center has shown that DEPG can also remove some of the tars present in syngas from fluid-bed gasification of biomass feedstocks, with heavier hydrocarbons such as toluene, ethyl benzene, and naphthalene partitioning to the acid gas stream, while benzene generally remained in the treated gas stream.⁶⁶

⁶⁵ National Energy Technology Laboratory. (n.d.). MDEA. <https://netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/mdea>

⁶⁶ Stanislawski, J., Tolbert, S., Beddoe, C., Musich, M., Henderson, A., & Carriere, N. (2022, May 24). Biomass cofiring with precombustion carbon capture baseline testing at UND EERC. <https://doi.org/10.18141/1861421>

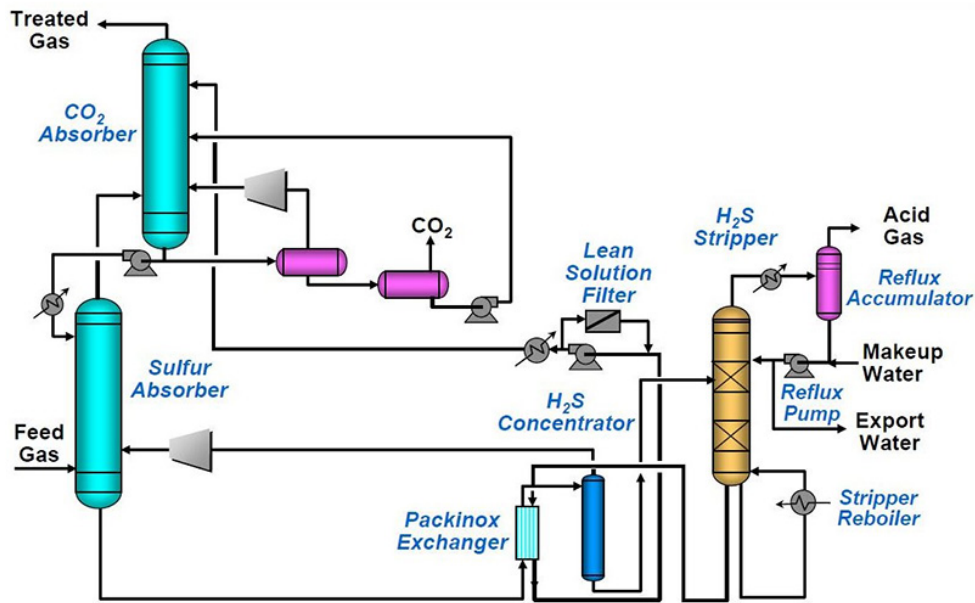


Figure 14: Generic two-stage Selexol process⁶⁷

Rectisol: Rectisol is another process using a physical solvent that is based on utilizing highly chilled methanol. At temperatures around -40°C , methanol has a high solubility for acid gas constituents including all forms of sulphur, tars, ammonia, HCN, and even elemental mercury. While the Rectisol process utilizes a relatively cheap and nonproprietary solvent, significant capital and operating costs are related to the large refrigeration load and the higher solvent losses associated with the higher vapor pressure of methanol. Vendors for the Rectisol process include Linde AG and Air Liquide. Gasification plants currently utilizing Rectisol include the Dakota Gasification SNG plant in Beulah, North Dakota; the Sasol Fischer-Tropsch plants in South Africa; and the Tennessee Eastman chemical plant in Kingsport, Tennessee. This process can remove CO_2 to well below 1 mol % in the deep-cleaned syngas, as well as reduce total sulphur to less than 0.1 ppm. Because of the high capital and operating cost and challenging heat integration, Rectisol would only be considered cost-competitive for the largest-scale biomass gasification projects.

Sulfinol: Sulfinol is considered both a physical- and chemical-type solvent since it consists of a mixture of diisopropanol amine or methyl diethanolamine (30-45 %), tetrahydrothiophene dioxide (40-60 %), and water (5-15 %). This combination provides a higher acid gas loading in the solvent and has a lower regeneration energy requirement than the amine-only-based solvent systems, though steam is still required for the regeneration process. Compared to physical solvents, Sulfinol has significantly less co-absorption of hydrocarbons. The Sulfinol process is provided by Shell and was used on the Buggenum Netherlands IGCC plant (Figure 15). The process can be selective to the removal of sulphur as H_2S , COS, and mercaptans, or it can be adapted to remove bulk CO_2 .

⁶⁷ National Energy Technology Laboratory. (n.d.). Selexol. <https://netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/selexol>

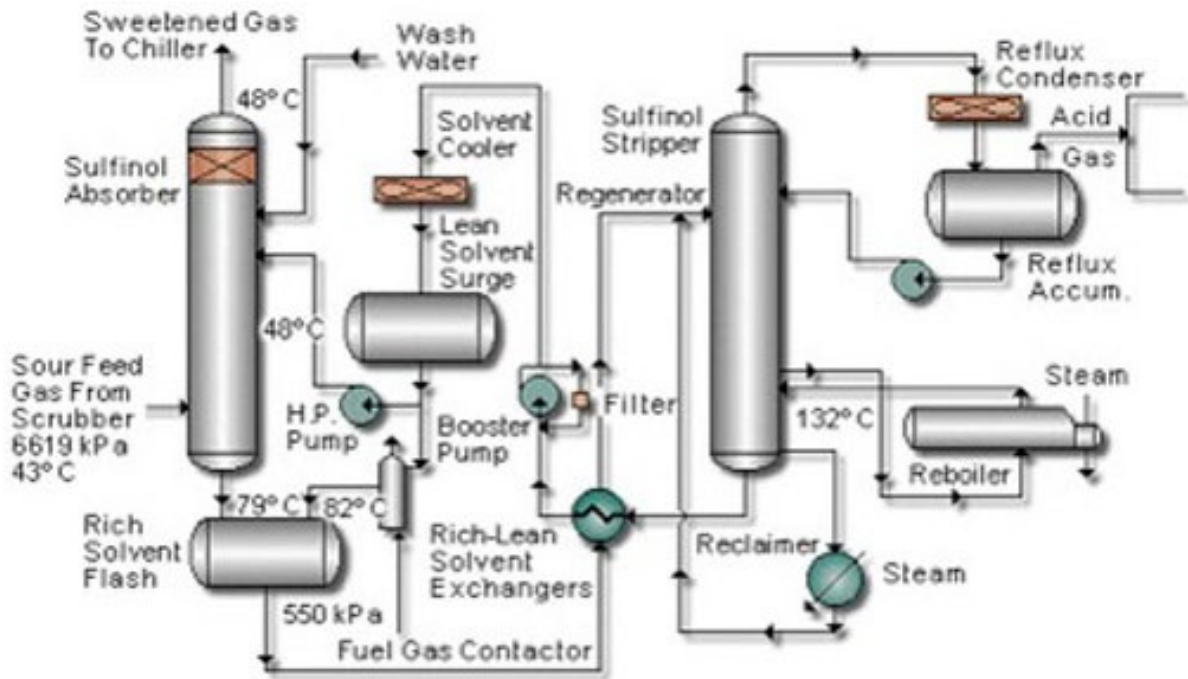


Figure 15: Sulfinol process⁶⁸

LO-CAT: Another low-temperature solution-based sulphur removal and recovery process is the LO-CAT technology offered by Merichem. This technology utilizes a proprietary chelated iron liquid redox catalyst that converts H_2S to solid elemental sulphur by carrying out the direct oxidation of H_2S . In the first step, H_2S is absorbed into water, where it reacts with ferric iron (Fe^{+3}) to form elemental sulphur and ferrous iron (Fe^{+2}). The solution is then oxidized under air to convert the ferrous iron back into ferric iron for further sulphur recovery, and elemental sulphur is recovered as a solid cake using a filtration system. Unlike DEPG or Rectisol (which capture CO_2 and other components), LO-CAT is specific to H_2S and has demonstrated H_2S removal efficiencies of more than 99.9 %, achieving sulphur levels as low as 1 ppm.

In the LO-CAT DirectTreat process (Figure 16), absorption occurs at elevated pressures of up to 300 psig, and the solution is then reoxidized in a separate vessel at lower pressure. Solution is circulated through the filtration system for solid sulphur recovery, and the oxidized solution is pumped back into the absorber vessel. A washing step (not shown) is utilized to recover as much of the catalytic solution as possible. The recovered sulphur cake exhibits small particle sizes with soft texture and high surface area that supports microbial action in soil, with the sulphur cake having been successfully used as a soil amendment since the 1990s. Sulphur removal capacities from 0.5 to 25 tons/day have been demonstrated, with more than 200 systems being utilized.

⁶⁸ National Energy Technology Laboratory. (n.d.). Sulfinol. <https://netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/sulfinol>

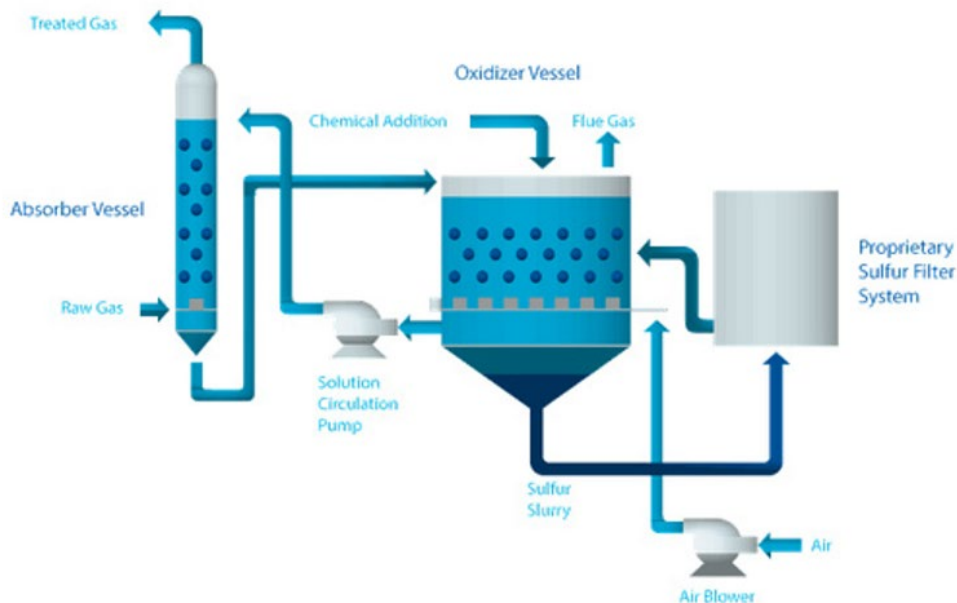


Figure 16: LO-CAT DirectTreat process flow diagram⁶⁹

2.3.2.3. Solid Sorbents

Several catalyst vendors make solid sorbents that will capture H₂S and other sulphur species from syngas. These sorbents are generally metals that react with the sulphur species to form a metal sulfide. Zinc-based metal sorbents are frequently utilized, although other metals can be utilized or co-blended with zinc to improve sulphur capture efficiencies. Some sorbents are regenerable, while others are a single-use product, depending on the sorbent chemistry and other process parameters.

Regenerable and Non-Regenerable Sorbents: Regenerable sorbents are commercially available as either pellets for fixed-bed operation or as a powder suitable for fluid-bed/circulating fluid contactors. In regenerable reactors, sorbent that has been saturated with sulphur is heated in a dilute oxygen-containing stream, which converts the metal sulfide back to an oxide while releasing sulphur as SO₂. Regenerable sorbents need to be robust enough that they can be regenerated without excessive attrition, and reactor materials must be suitable for exposure to acidic vapours that form from sulphur oxidation.

RVS-1 from Clariant is a durable, regenerable, and efficient sorbent pellet designed primarily to remove sulphur species from high-temperature fuel gas for environmentally safe and energy-efficient system operations. RVS-1 is designed for use in both fixed-bed and intermittent moving bed applications. This sorbent works best between 290 °C and 540 °C and at pressures from ambient up to 50 bar. The recommended space velocity is less than 2,000/h. Regeneration is recommended at low pressure in a stream containing 2 % oxygen. The sorbent-bed temperature needs to be increased to about 560 °C-600 °C prior to oxidation, with the bed temperature increasing to about 675 °C-730 °C during the regeneration process. The SO₂ stream generated during oxidation is very amenable to a sulphuric acid recovery process to produce salable sulphur product.

Through U.S. Department of Energy funding, Research Triangle Institute has developed an attrition-resistant fluidizable bed sorbent called RTI-3 for the deep desulphurization of syngas at warm gas conditions. This regenerable sorbent was demonstrated at a 50-MW scale at the Tampa Electric IGCC

⁶⁹ TAS Environmental Services. (2023, September 12). LO-CAT® maintenance. <https://www.taslp.com/lo-cat-maintenance/>

plant⁷⁰ utilizing a twin circulating fluidized-bed system that would contact the sorbent with syngas in one loop and regenerate a slipstream of the sorbent in the other leg of the twin circulating fluid-bed contactors. Figure 17 is a schematic of the warm-temperature syngas desulphurization process depicting the twin loop configuration. An advantage of this system over the use of fixed beds is the continuous withdrawal and regeneration of a portion of the sorbent, preventing the need to cycle through beds as they become saturated. The circulating fluid-bed contactor also results in a very high syngas throughput per unit cross-section area, thereby reducing the capital cost for larger plants. More than 5,000 hours have been demonstrated at the 50-MW scale. The Energy & Environmental Research Center has also tested this sorbent in pilot-scale test systems with similar results in which total sulphur concentrations were reduced to less than 10 ppm.⁷¹ This syngas was then easily polished to less than 0.2 ppm with commercially available single-use sorbents. Larger biomass systems feeding material with appreciable sulphur are likely to benefit from the high-throughput contactor, while smaller biomass systems or feeds with only traces of sulphur will more likely be favoured by the fixed-bed sorbent contactor systems due to reduced complexity and reactor height/size.

Non-regenerable solid sorbents are provided by several vendors, including Clariant (Actisorb), Johnson Matthey (Puraspec), and Haldor Topsoe (HTZ). These vendors have sorbents for both bulk sulphur removal and specially formulated polishing sulphur sorbents that will further reduce the total sulphur concentrations to well below 1 ppm.

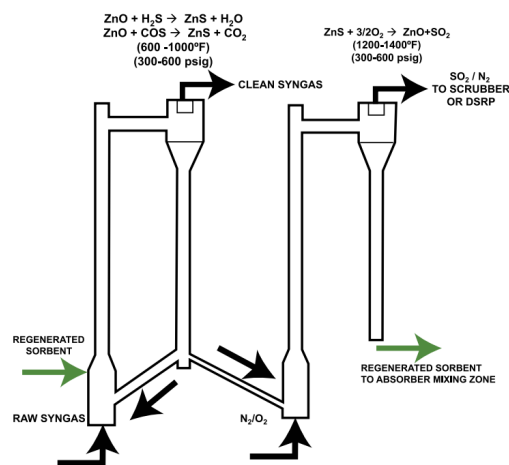


Figure 17: RTI warm-temperature syngas desulphurization process⁷²

Sulphur Recovery: Except in the case of non-regenerable sulphur sorbents, all sulphur removal processes for syngas treating will generate sulphurous off-gases where the sulphur must be recovered and (ideally) converted into saleable products such as elemental sulphur or concentrated sulphuric acid. The main processes utilized are the Claus process to convert H₂S into elemental sulphur or the wet sulphuric acid process to produce a concentrated sulphuric acid byproduct.

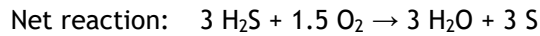
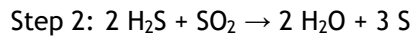
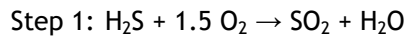
The basic Claus process for substoichiometric combustion of H₂S to elemental sulphur follows the following

⁷⁰ Howe, G., Albritton, J., Turk, B., Denton, D., & Gupta, R. (2018, January). RTI warm syngas cleanup operational testing at Tampa Electric Company's Polk 1 IGCC site [Final scientific/technical report]. <https://doi.org/10.2172/1419426>

⁷¹ Stanislawski, J. J., & Laumb, J. D. (2008, July). Gasification of lignites to produce liquid fuels, hydrogen, and power, year 1 final report (Report No. 2008-EERC-07-03). Energy & Environmental Research Center

⁷² RTI International. (n.d.). RTI and Eastman Chemical demonstrate warm-temperature syngas cleanup technology. <https://www.rti.org/brochures/rti-and-eastman-chemical-demonstrate-warm-temperature-syngas-cleanup-technology>

reactions:



Approximately one-third of the H_2S is converted to SO_2 by direct combustion with oxygen. This SO_2 then reacts with the remaining H_2S to form elemental sulphur. Figure 18 depicts a process schematic for a simple Claus system. An initial-reaction furnace operates at temperatures of around $1,050^\circ\text{C}$, with 60-70 % of the sulphur recovered in an outlet condenser. The remaining gas is reheated to above 300°C , and the process is continued through several catalytic stages with temperature reduction and molten sulphur removal between each stage. Catalyst is typically activated alumina or titanium oxide. Although lower temperatures favour sulphur conversion, the temperature in each stage must be kept high enough to prevent condensation in the catalyst pores, which would lead to deactivation. Depending on the number of catalyst beds, sulphur recovery can range from 92 % up to 97 %.

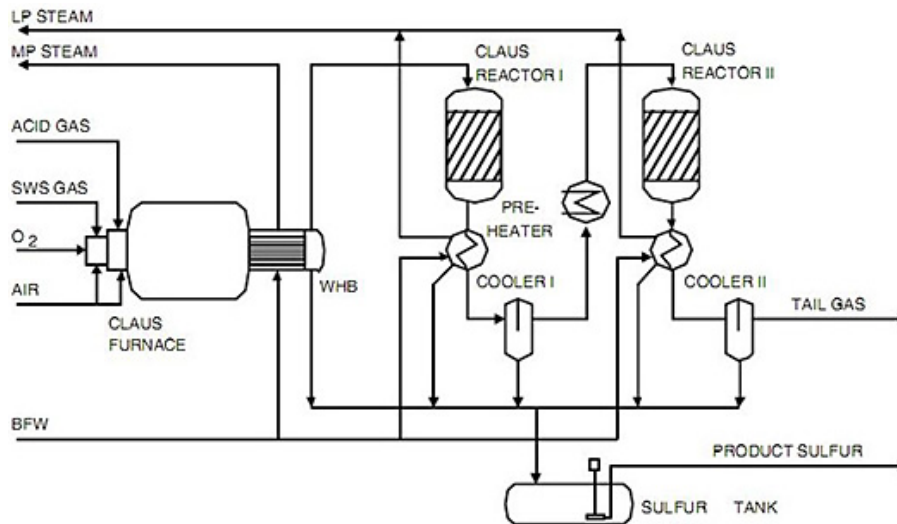


Figure 18: Simplified Claus process for elemental sulphur recovery⁷³

Tail gas from the Claus process contains 0.8-1.5 % residual sulphur and was historically incinerated. As air emissions limits have tightened over the years, most Claus processes have added some type of tail gas treating processes to reduce the total sulphur emitted to very low ppm levels. Among these tail gas treating options is the Shell Claus Off-Gas Treating (SCOT) process. As depicted in Figure 19, tail gas is reheated with a substoichiometric in-line burner before passing to a catalytic hydrogenation reactor, which converts all the sulphur back to H_2S . The gas is scrubbed with an amine solution to capture the H_2S , which is then recovered as acid gas in a separate stripper column and recycled to the Claus process. Other tail gas treating processes include ExxonMobil Flexsorb and BASF's OASE Sulfexx process. Total sulphur removals of up to 99.9 % are achievable using tail gas treating.

⁷³ National Energy Technology Laboratory (NETL). (n.d.). SCOT Tail Gas Treating. Retrieved August 2023, from <https://netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/scot-tgtu>

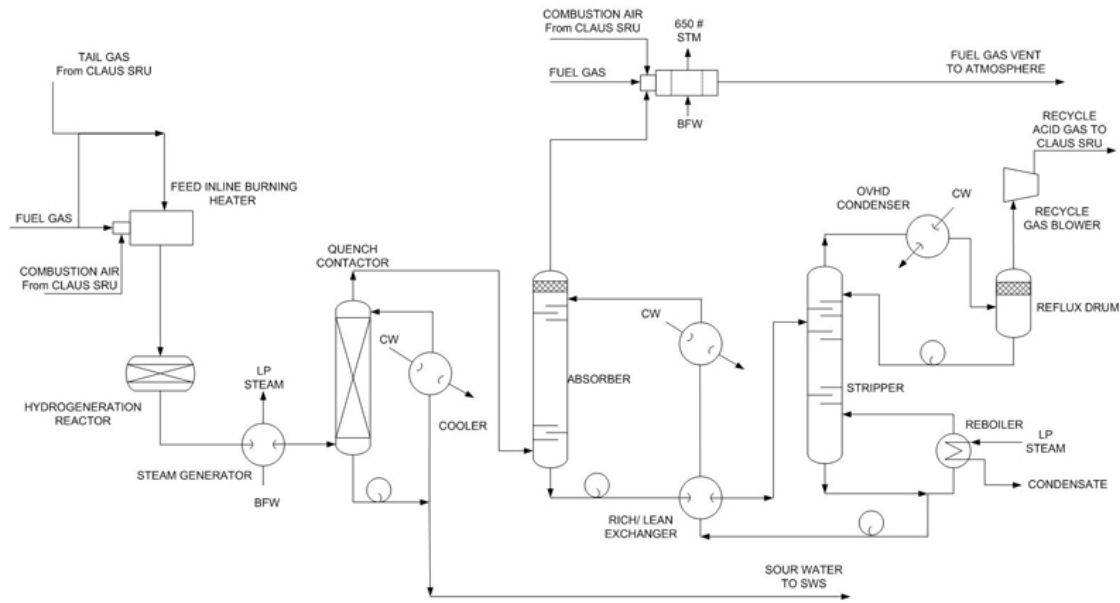


Figure 19: SCOT tail gas treating process schematic⁷⁴

Another sulphur recovery process is the wet sulphuric acid process developed by Haldor Topsoe. This process can be utilized to directly treat the acid gas stream from a solvent-based sulphur removal process or applied to the tail gas from a Claus process.

The main reactions in the wet sulphuric acid process are:

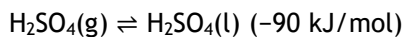
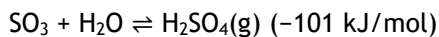
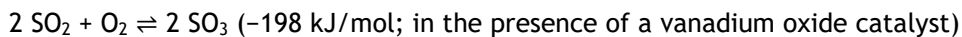
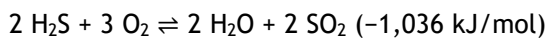


Figure 20 depicts a process flow schematic for the wet sulphuric acid process. In this process, the acid gas is combusted to convert all the sulphur to SO_2 and then cooled to approximately 430°C while generating steam. The cooled flue gas passes through a vanadium-based catalyst reactor, where the SO_2 is converted to SO_3 . Because the reactions involved are highly exothermic while equilibrium favours temperatures below 400°C , intermittent heat recovery using air cooling between catalyst beds is utilized to achieve high conversion to SO_3 . The SO_3 reacts with water vapor to form vapor-phase sulphuric acid, which then condenses downstream as concentrated sulphuric acid. All the process piping is specially designed to handle the acidic nature of the process streams. The energy released is used to produce approximately 2-3 tons of high-pressure steam per ton of acid.

⁷⁴ National Energy Technology Laboratory (NETL). (n.d.). SCOT Tail Gas Treating. Retrieved August 2023, from <https://netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/scot-tgtu>

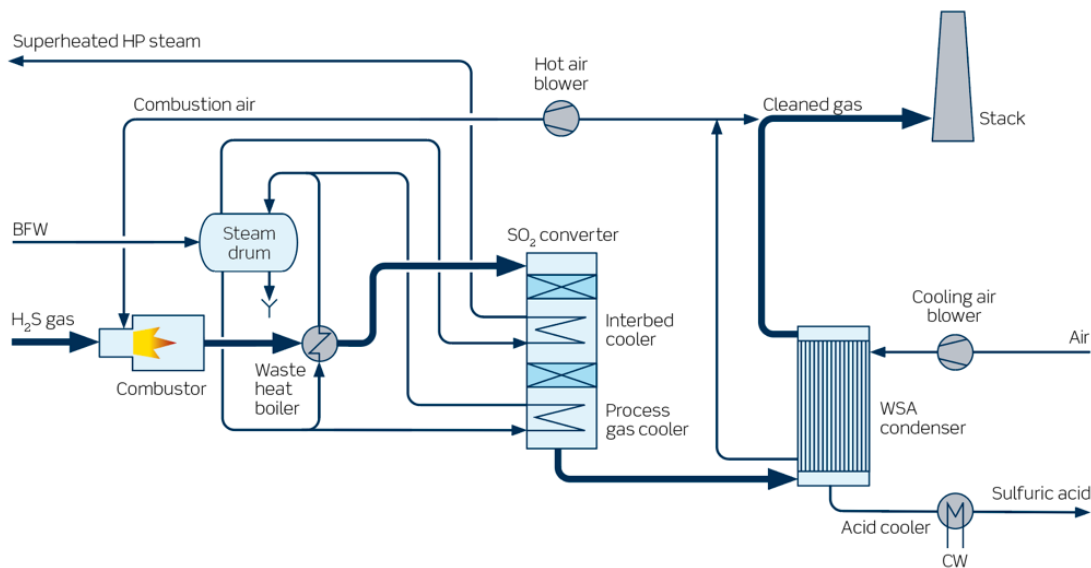


Figure 20: Generic wet sulphuric acid process schematic⁷⁵

2.4. AMMONIA REMOVAL

Depending on the specific feed type, biomass can contain relatively high levels of nitrogen. Most of the fuel-bound nitrogen in a solid feedstock is converted to ammonia during gasification, producing a raw syngas that may contain ammonia above 1,000 ppm. Since ammonia is very water soluble, a water scrubber will reduce ammonia in the syngas to less than 10 ppm while also removing most of moisture and tar. For most chemical production processes, the use of a water scrubber system is likely before syngas would undergo conversion to products such as Fischer-Tropsch liquids, methanol, and renewable natural gas. Water-gas shift catalysts are not sensitive to ammonia, allowing syngas to be shifted at warm temperatures to properly adjust hydrogen concentration prior to water scrubbing.

In some cases, it may be desirable to catalytically remove ammonia without a water wash. Catalytic decomposition of ammonia can approach equilibrium at very high temperatures and low pressures. This option is not desirable for chemical or fuel synthesis since most synthesis processes require high pressures, but it may be an option for low-pressure fuel gas production or for situations in which syngas is to be compressed after treatment. Approximately 90 % catalytic decomposition of NH_3 has been demonstrated over a nickel-based Haldor Topsoe high-temperature steam-reforming (HTSR-1) catalyst at 800°C .⁷⁶ Enviropower tested nickel- and ruthenium-based catalyst in the range of 370°C - 480°C , reportedly approaching equilibrium ammonia conversion of 99 % with gas residence times of 1-2 seconds.⁷⁷ Johnson Matthey offers commercial Katalco 27 brand ammonia cracking catalysts which, although intended for concentrated streams of ammonia, could crack more dilute streams of ammonia in low-pressure syngas.

2.5. CHLORINE REMOVAL

Biomass and waste material may contain appreciable levels of chlorine, and chlorine control can be a serious consideration when utilizing syngas derived from gasification of these feedstocks. Conventional

⁷⁵ Topsoe. (n.d.). Wet Gas Sulphuric Acid (WSA) Technology. Retrieved August 2023, from <https://www.topsoe.com/our-resources/knowledge/our-products/process-licensing/wet-gas-sulphuric-acid-wsa-technology>

⁷⁶ Gangwal, S. K., Gupta, R. P., Portzer, J. W., Turk, B. S., Krishnan, G. N., Hung, S. L., & Ayala, R. E. (1996). Catalytic ammonia decomposition for coal-derived fuel gases [Technical Report]. Morgantown Energy Technology Center. <https://doi.org/10.2172/419973>

⁷⁷ Mojtahedi, W., Ylitalo, M., Härkönen, M., Maunula, T., Luoma, M., Abbassian, J., & Wangerow, J. (1995). Catalytic decomposition of ammonia [Technical Report]. Combustion Chemistry Research Group, Finland

water scrubbers have been shown to be effective at removing chlorine as HCl to less than 1 ppm. For systems recirculating water through a scrubber, this chloride can concentrate, and water treatment may be required to reduce the chlorine concentration in the wastewater stream.

Numerous catalyst vendors have developed various guard bed sorbents for protecting catalysts from poisons such as chlorine. These vendors include Haldor Topsoe (HTG-10), Clariant (Actisorb Cl), and Johnson Matthey (Puraspec Clear and Purasieve). Actisorb Cl is a ZnO-based sorbent that operates at warm gas temperature suitable for shift catalyst operation. Puraspec Clear and Purasieve are bimetallic sorbents for both HCl and organic Cl removal. Sodium-based sorbents such as trona and nahcolite have also been shown to reduce chlorine to very low levels in gas streams at 350°C-500°C. These sorbents have fairly low eutectic melting temperatures and need to be operated at reduced temperature.

3. New Developments in Syngas Cleaning

New technologies for producing clean syngas from biomass are continuing to be developed to respond to the need for a clean or ultra-clean product to meet stringent requirements for downstream unit operations. Catalysts for in situ tar cracking and reforming are being developed with longer lifetimes and reduced susceptibility to poisoning and attrition. Novel reactor designs employing the use of hot oxygen at the reactor exit are also being tested as a means of process intensification. Small-scale modular plasma reactors are being developed by Heartland Technologies (and others) where the scale is suitable for deployment at scales that are more suited to the biomass or waste carbon resource (hundreds to 2,000 tonnes per day). Work is also being done on the use of nonthermal plasma reactors coupled with heterogeneous catalysts. These reactors operate at 300°C-500°C as opposed to thermal plasma reactors that operate up to 7,000°C, thus requiring much less energy and facilitating use of catalysts in the reactor to make the chemistry more efficient and selective. Frontline BioEnergy has recently reported on an innovative technology, called TarFreeGas, that has achieved ultra-clean biomass-derived synthesis gas with a combination of their gasification technology and a novel catalytic gas converter. Few details concerning the catalytic converter are available, but tar levels are said to be 'non-detectable'.

Generally, the transition from utilizing clean biomass from agriculture (e.g., short-rotation crops, straw) and forestry to the necessity to utilize residues and waste materials makes the syngas cleaning tremendously more complex due to poisoning of catalysts, blocking of membranes or filters, and increased loads of impurities such as heavy metals and ash constituents. The following subsections provide some aspects for new developments, with a special focus on tar removal, since this is one of the main barriers for commercial application of gasification for syngas applications.

3.1 THERMAL CRACKING OF TARS

Generally, these methods can be again divided into in situ and ex situ measures. Generally, downstream measures are necessary to gain reasonably low tar values in the producer gas. Thermal cracking or plasma tar cracking downstream of a gasifier and the partial oxidation method are widely discussed in the literature.⁷⁸ At elevated temperatures with sufficient residence time, organic compounds, especially tars, can be decomposed into smaller compounds, ideally permanent gases. Although at higher temperatures negative effects such as formation of nitrogen oxides and recombination of tars can be expected, temperatures above 1,250°C and residence times higher than 0.5 seconds are suggested in the literature.⁷⁹ Thermal cracking is typically performed in inert atmosphere, whereas partial oxidation obviously needs a certain oxygen level. For partial oxidation, the temperature is increased by the injection of oxygen or air to provide the activation energy to crack aromatic hydrocarbons or hydrocarbon chains. However, the injection of oxygen can lead to the oxidation of valuable product gas components such as hydrogen or produce unwanted impurities such as polyaromatic hydrocarbons or even soot. Although partial oxidation could be done in situ in the gasifier, it is mainly done in a secondary reactor. For in situ systems, process designs other than introducing oxygen as a gasification agent are discussed in the literature—for example, application of oxygen transporting membranes⁸⁰ and a two-stage gasification system.⁸¹ Generally, partial oxidation systems are relatively simple for the implementation but need either pure oxygen or dilution of the synthesis gas with nitrogen. Moreover, valuable product components

⁷⁸ Deng, C., Song, W., Chai, Z., Guo, S., & Zhu, Z. (2020). Characteristics of tar thermal cracking and catalytic conversion during circulating fluidized bed char gasification. *Energy & Fuels*, 34, 142-149

⁷⁹ Han, J., & Kim, H. (2008). The reduction and control technology of tar during biomass gasification/pyrolysis: An overview. *Renewable and Sustainable Energy Reviews*, 12, 397-416

⁸⁰ Aguilera, L. M., Puig-Arnavat, M., Ovtar, S., Gorauskis, J., Ahrenfeldt, J., Henriksen, U. B., et al. (2023). Partial oxidation of biomass gasification tar with oxygen transport membranes. *Journal of Membrane Science*, 681, 121769

⁸¹ Ahrenfeldt, J., Egsgaard, H., Stelte, W., Thomsen, T., & Henriksen, U. B. (2013). The influence of partial oxidation mechanisms on tar destruction in TwoStage biomass gasification. *Fuel*, 112, 662-680

are oxidized as well, which leads to reduced efficiency of the overall process.

Technically even more complex is the application of thermal plasma, ideally downstream of the gasifier, with temperatures above 2,000 °C. Typically, the plasma is provided electrically and requires a substantial amount of energy; reliable figures on energy requirements are largely missing in the literature. These technologies are typically used for problematic feedstock materials such as hazardous waste materials (e.g., hospital waste). On the benefits side, a very clean syngas, mainly consisting of hydrogen and carbon monoxide and free of tars, is gained. Moreover, a molten slag with typically all impurities captured (e.g., heavy metals, alkali metals) is produced.

For the application of plasma into gasification processes, different concepts of two-stage gasification are available. Residues and waste materials are converted in a gasifier followed by a second stage with a plasma being introduced to clean the producer at high temperatures. The combination of pyrolysis in a grate-fired boiler at temperatures up to 600 °C and plasma is called the Plasco process. This process has been demonstrated at a scale of 135 tons per day.⁸² Materazzi and coauthors published results with a two-stage system, using a bubbling fluidized-bed gasifier being operated with oxygen-steam mixtures followed by a plasma converter. The feedstock is refuse-derived fuel, and the temperatures in the plasma converter reached about 1,200 °C to gain full conversion of hydrocarbons to syngas. Although these large-scale demonstration plants showed promising results, most of the research on plasma for downstream gas cleaning is on laboratory-scale investigations. Many researchers investigate the combination of plasma and catalytic tar removal. Obviously, addition of steam enhances the tar destruction rates but does not provide 100 % conversion efficiencies.⁸³

3.2 CATALYTIC GAS CLEANING

Similar to the thermal tar cracking methods, catalytic tar removal systems are possible as in situ or ex situ measure. Generally, the main aim is to remove tar, and only on the second hand to improve the gas quality and recover the energy of the tars, which is roughly in the order of 1-3 % of the chemically bound energy in the feedstock. Integration of catalytic processes into thermochemical conversion process improves the overall efficiency of the whole process and is intended to reduce the costs.

Research and development on catalytic tar removal has been ongoing for several decades, but state-of-the-art examples are rarely available. One reason is that most of the research is done under strongly idealized conditions (either short-term tests or even using model gas and/or tar substances). In reality, catalyst lifetime is negatively influenced by mechanical and thermal stress, as well as deactivation by catalyst poisons. Due to dust, ash, and char particles, the catalytic surface of catalysts can be destroyed due to attrition or blockage of active sites. Furthermore, catalyst poisons such as Cl, S, or heavy metals can attach to the catalytic sites and therefore deactivate the catalyst, even in very small amounts (ppm to ppb level). One successful development is the tar reforming catalyst from Haldor Topsoe.⁸⁴

Many different reactions take place in parallel such as cracking, steam and dry reforming, shift reactions, and partial oxidation. With regard to the catalytic component(s), several classifications are used in the literature, but in the respective literature they are divided into (1) alkali metals, (2) non-metallic oxides, and (3) supported metallic oxides, whereas each of these components can be theoretically applied with in situ and ex situ methods. Nevertheless, if attrition plays a major role, expensive and/or synthetically

⁸² Waldheim, L. (2018). Gasification of waste for energy carriers: A review. Retrieved August 2023, from <https://www.ieabioenergy.com/wp-content/uploads/2019/01/IEA-Bioenergy-Task-33-Gasification-of-waste-for-energy-carriers-20181205-1.pdf>

⁸³ Materazzi, M., & Taylor, R. (2019). Plasma-assisted gasification for waste-to-fuels applications. *Industrial & Engineering Chemistry Research*, 58, 15902-15913

⁸⁴ Andersson, K. J., Skov-Skjøth Rasmussen, M., & Højlund Nielsen, P. E. (2017). Industrial-scale gas conditioning including Topsoe tar reforming and purification downstream biomass gasifiers: An overview and recent examples. *Fuel*, 203, 1026-1030

complex materials are typically limited to ex situ reactor concepts.

The following paragraphs briefly describe the different groups of catalysts with specific mention of selected concepts. Alkali and alkaline earth metals are the main parts of the ash in biomass feedstocks, and depending on the origin and type of biomass, the values can differ significantly. Generally, these components act during the devolatilization phase, as well as during the gasification as such to reform tars. Moreover, kinetics and reactivity, as well as a shift in equilibria, are influenced, whereas for some applications even more alkali and alkaline earth metals are added to the feedstock. Depending on the specific constituents, negative effects are well known such as ash melting and therefore particle agglomeration and slagging (mainly if sodium and potassium are present). For fluidized-bed applications, even deactivation of potentially catalytic surfaces of the bed material (e.g., olivine, limestone) is reported due to alkali and alkaline earth metal layer formation.

The group of non-metallic oxides is mainly covered by calcites (CaO) and magnetites (MgO), and positive effects on tar cracking are well known. In uncalcined form, which is not catalytically active, these materials are called limestone (CaCO₃), magnesium carbonate (MgCO₃), and dolomite (MgCO₃·CaCO₃). This group of catalysts is widely available at low costs and is easy to dispose of. However, most of these materials differ significantly in their properties (especially in attrition resistance) for different origins, although the chemical structure is the same. Especially for in situ application in fluidized-bed systems, attrition and deactivation due to surface sintering is a major concern. Although these negative effects are well known, one special process application called ‘sorption-enhanced reforming’ recently gained increased interest (Figure 21). The main idea behind this concept is to use a dual-fluidized bed gasification concept and operate the gasification zone at temperatures below 700 °C with CaO as bed material to capture CO₂ and furthermore remove CO because of the homogeneous water-gas shift reaction. The calcined bed material (CaCO₃) is transported to a combustion zone operated at temperatures above 900 °C to release the CO₂.⁸⁵ Thus, high hydrogen fractions are gained in the producer gas, and despite the low gasification temperature, very low tar levels (approximately 1 g/Nm³ gravimetric tar, 5 g/Nm³ GCMS tar) have been reported due to the catalytic effect of CaO.⁸⁶ Moreover, if the combustor is operated under oxy-fuel conditions, even pure CO₂ can be provided (Figure 22).

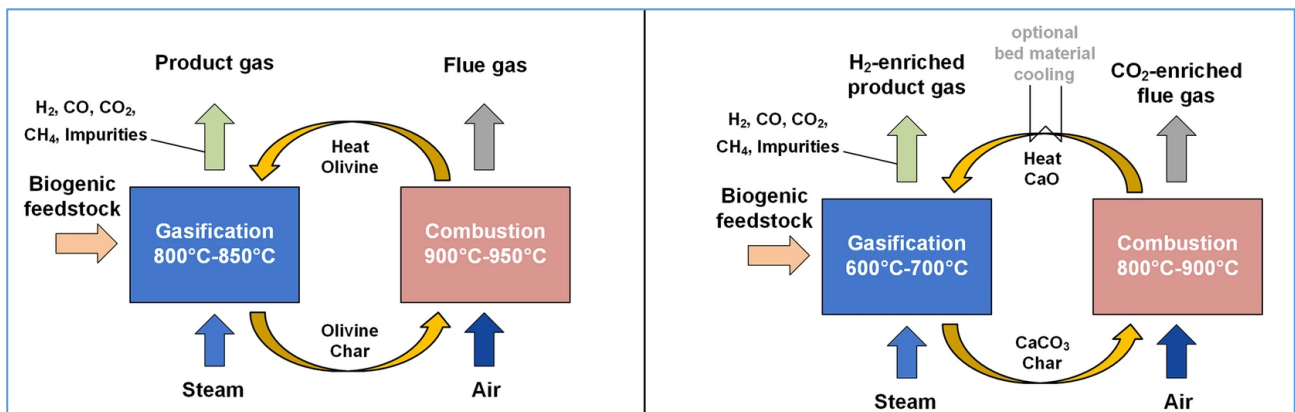


Figure 21: Principle of dual-fluidized bed gasification (left) and sorption-enhanced reforming (right)

⁸⁵ Koppatz, S., Pfeifer, C., Rauch, R., Hofbauer, H., Marquard-Moellenstedt, T., & Specht, M. (2009). H₂ rich product gas by steam gasification of biomass with in situ CO₂ absorption in a dual fluidized bed system of 8 MW fuel input. *Fuel Processing Technology*, 90, 914-921

⁸⁶ Fuchs, J., Schmid, J. C., Müller, S., & Hofbauer, H. (2019). Dual fluidized bed gasification of biomass with selective carbon dioxide removal and limestone as bed material: A review. *Renewable and Sustainable Energy Reviews*, 107, 212-231

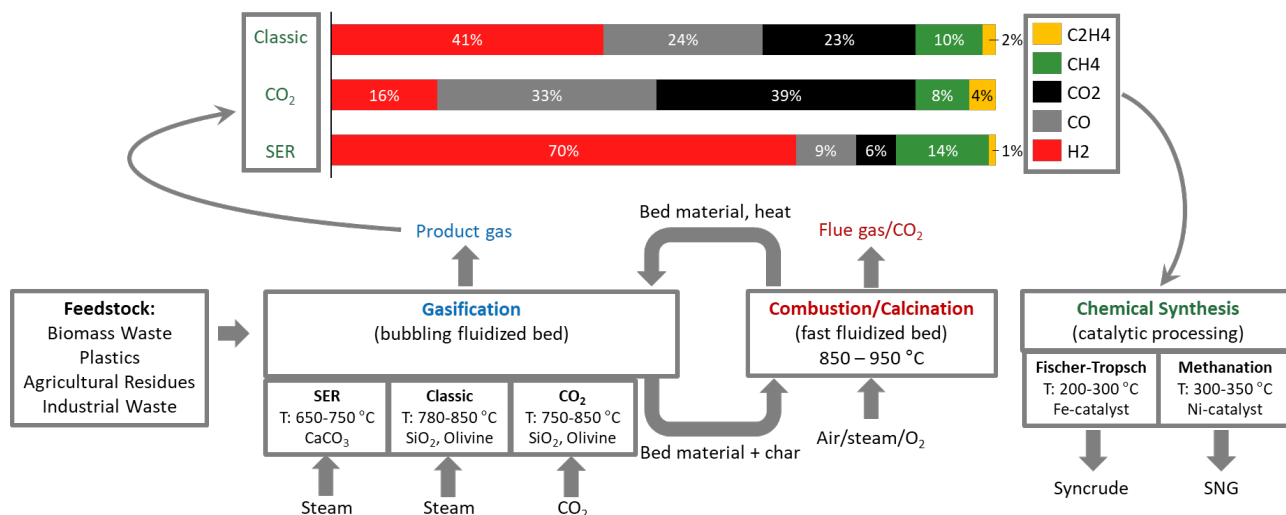


Figure 22: Overview on process design and achieved gas qualities

Supported metallic oxides are widely investigated and discussed as catalytic component for product gas upgrading, especially for reforming of tars and gaseous hydrocarbons. Dry and steam-reforming reactions are catalysed by elements from the transition and noble metal group such as Ni, Pt, Rh, or Ru, whereas nickel is the best investigated due to reasonable costs and conversion efficiency. Again, application as in situ or ex situ reformer is possible with easier application downstream of the gasifier. Positive results are achieved in laboratory investigations, but applications with real producer gas prove several limitations such as deactivation or poisoning by impurities such as sulphur compounds, heavy metals, alkali metals, or even halogens, and already low values (ppm or even ppb levels) can significantly reduce the lifetime of the catalysts. One success story is combination of a monolithic ZrO_2 in combination with a noble metal catalyst as pre-reformer followed by a fixed-bed final reformer with a nickel catalyst. This setup has been recently tested in a process development unit by VTT Finland for 215 hours of operation without loss of activity;⁸⁷ 98 % of tars and 92-99 % of benzene was decomposed. Practically no deactivation due to carbon deposits or poisoning was recorded. The same system has been tested in a commercial gasifier in Varkaus (Finland) in a 5-MW slipstream of a 12-MW fuel input plant. No loss of activity over 5,500 hours of operation was reported.⁸⁸

3.3 ADVANCED METHODS FOR SELECTIVE SYNGAS OPTIMIZATION

Depending on the final utilization step, different options for removal of unwanted gas components (e.g., CO_2 if hydrogen is the main product) are available: pressure swing adsorption, cryogenic separation/distillation, and membrane separation. The following subsections provide new developments on these techniques.

3.3.1 Membrane Separation

Membranes allow fast and with relatively low energetic efforts to separate gas flows based on their permeability and selectivity. The driving force is typically a difference in pressure or concentration, supported by temperature adjustment. The main membrane materials are polymers and metals, but in the field of upgrading of synthesis gas, novel materials are mentioned in the literature such as nanomaterials, molecular sieves, or metal-organic frameworks. The following membrane types are discussed:

⁸⁷ Kurkela, E., Kurkela, M., & Hiltunen, I. (2016). Steam-oxygen gasification of forest residues and bark followed by hot gas filtration and catalytic reforming of tars: Results of an extended time test. *Fuel Processing Technology*, 141, 148-158

⁸⁸ Hiltunen, I., Tuomi, S., & Kurkela, E. (2022). The role of catalytic reforming in the production of synthesis gas from biomass and waste. TCbiomass, Denver USA

electrochemical hydrogen pumping membranes, ionic liquid-based membranes, inorganic membranes, and carbon-based membranes.

Inorganic membranes. This type of material can be used to enhance the purity of hydrogen (e.g., from sorption-enhanced reforming processes) using the sorption-diffusion mechanism (e.g., based on palladium). Although other materials are mentioned as well (Nb, V, and Ta), palladium is the most widely used basic material because it offers high hydrogen selectivity, high resistance to hydrogen fluidity, and auto-catalytic hydrogenolysis reactions.⁸⁹ Actual research is focusing on the stability of such membranes.

Carbon-based membranes. Two different types of membranes within this group are reported: carbon molecular sieve membranes and supported carbon membranes. The first are produced through carbonization of polymeric precursors, and the second are produced by depositing a thin film on a support (metallic or ceramic). Both offer high selectivity of hydrogen versus the other gaseous components.

Ionic liquid-based membranes. This kind of membranes is based on ionic liquids, which are liquids at ambient conditions or solids with melting temperatures below 100°C. The specific application of this kind of membrane is, for example, the separation of CO₂ from complex gas mixtures. Different types of this kind of membrane are reported in the literature.^{90,91}

Electrochemical hydrogen pumping membranes. This type of membrane was first presented in the mid-1960s. It is basically an electrochemical setup with an anodic and a porous electrode. The protons are selectively pumped through the proton-conducting membrane, and the electrons reach the cathode through an external circuit. The protons and electrons recombine at the cathode to produce high-purity molecular hydrogen. Different membrane materials are reported in the literature such as polybenzimidazole, perfluorinated sulfonic acid, etc.

3.3.2 Pressure Swing Adsorption

This group of techniques is not new, but the application for separation of gases from gas mixtures produced by biomass gasification is somewhat new and requires additional development. The purification separation step depends on the adsorbent's capacity and operating pressure, as well as the strength of adsorption. In one typical application, hydrogen can be separated since other gasification gas components are typically less adsorbed on the adsorbents and pass through the separator. Reviews are available in the scientific literature to show possible pathways.^{92,93,94}

3.3.3 Cryogenic Separation

The main principle of these separation procedures is to use the effect of different boiling points of the different gas components and separate these components by cooling. To remove hydrogen from producer gas from gasification, the mixture needs to be cooled to temperatures below -150°C.⁹⁵ Thus, this kind of

⁸⁹ Nakatsuji, H., & Hada, M. (1985). Interaction of a hydrogen molecule with palladium. *Journal of the American Chemical Society*, 107, 8264-8266

⁹⁰ Yan, X., Anguille, S., Bendahan, M., & Moulin, P. (2019). Ionic liquids combined with membrane separation processes: A review. *Separation and Purification Technology*, 222, 230-253

⁹¹ Rabiee, H., Ghadimi, A., & Mohammadi, T. (2015). Gas transport properties of reverse-selective poly(ether-b-amide6)/[Emim][BF₄] gel membranes for CO₂/light gases separation. *Journal of Membrane Science*, 476, 286-302

⁹² Shabbani, H. J. K., Othman, M. R., Al-Janabi, S. K., Barron, A. R., & Helwani, Z. (2024). H₂ purification employing pressure swing adsorption process: Parametric and bibliometric review. *International Journal of Hydrogen Energy*, 50(Part A), 674-699

⁹³ Luberti, M., & Ahn, H. (2022). Review of Polybed pressure swing adsorption for hydrogen purification. *International Journal of Hydrogen Energy*, 47(20), 10911-10933

⁹⁴ Zhu, X., Li, S., Shi, Y., & Cai, N. (2019). Recent advances in elevated-temperature pressure swing adsorption for carbon capture and hydrogen production. *Progress in Energy and Combustion Science*, 75, 100784

⁹⁵ Voldsund, M., Jordal, K., & Anantharaman, R. (2016). Hydrogen production with CO₂ capture. *International Journal of Hydrogen Energy*, 41, 4969-4992

separation is cost- and energy-intensive to reach those temperatures, and moreover technically complex because of special material selection needed.

However, if the final product is pure hydrogen, a stepwise process can be performed such as partial condensation (Figure 23(a)) and a so-called methane wash (Figure 23(b)).⁹⁶

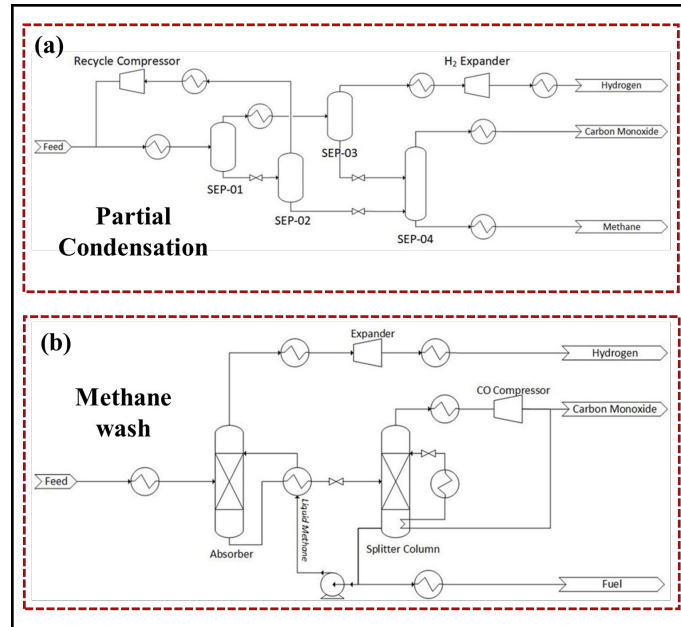


Figure 23: Process flow diagram for cryogenic separation of CO-CH₄ and H₂⁹⁶

⁹⁶ James, J., Lücking, L. E., van Dijk, H., & Boon, J. (2023). Review of technologies for carbon monoxide recovery from nitrogen-containing industrial streams. *Frontiers in Chemical Engineering*, 5, 1066091.

Conclusions

This report provides an in-depth exploration of gasification processes, as well as the challenges posed by impurities in the resulting producer gas. The introduction lays the groundwork by discussing the types of feedstock commonly used for gasification, followed by an analysis of the impurities that arise during gasification and their dependence on both the feedstock and the gasification technologies employed.

The report dives into various categories of gas-phase impurities, such as tars, nitrogen-containing compounds (e.g., NH_3 , HCN), sulphur-containing compounds (e.g., H_2S , COS), hydrogen halides (e.g., HCl), and trace metals. Each impurity group is discussed in terms of its formation mechanisms, its effects on downstream processes, and the specific challenges it presents to gas cleaning and syngas upgrading. The document emphasizes how the quality and type of feedstock, as well as operational parameters like temperature and pressure, significantly influence the composition and quantity of these impurities.

A key chapter of the report focuses on syngas cleaning technologies, detailing methods for removing particulates, metals, tars, sulphur, ammonia, and chlorine from the gas stream. Various approaches are evaluated, such as the use of bed additives, cold gas cleanup with solvents, and physical removal techniques like filtration and scrubbing. Specific attention is given to the technological advancements that improve the efficiency of these methods. Case studies, such as the example of Kew Technology, provide real-world applications of these cleaning technologies, illustrating how they are implemented in industry.

In addition to covering established methods, the report also reviews recent innovations in syngas cleaning. These include advanced techniques for tar removal, such as thermal cracking and catalytic gas cleaning, as well as emerging technologies for selective syngas optimization. Novel separation methods like membrane separation, pressure swing adsorption, and cryogenic separation are explored, showcasing their potential to improve the purification of syngas for specific applications, such as biofuel production and chemical synthesis.

The final chapters of the report cover the current status of producer gas cleaning and the future outlook for the field, emphasizing the ongoing development of technologies that can handle a wider variety of feedstocks and produce cleaner, more efficient syngas. Commercial technology providers for producer gas cleaning applications are shown in the appendix.

This detailed examination of gas cleaning technologies highlights the critical role of purification in ensuring the viability of gasification as a sustainable energy and chemical production process. As research continues to advance, these technologies are expected to evolve, meeting the growing demands of industrial applications and enabling cleaner, more efficient production systems.

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Appendix

Technologies for Removal of Impurities from Syngas - Companies List

Company	Removal Technology	Detailed Information	
Andritz	Tars (cracking/reforming)	Catalytic cracking and reforming (see VTT)	
Plasco		Plasma cracking	
Babcock & Wilcox Vølund	Tars physical removal	Water-based scrubbing including TARWATC	
Beth		Wet electrostatic precipitator filter	
CTU		RME-based scrubbing technology	
Dahlman		Oil-based scrubbing OLGA	
ECN		Oil-based scrubbing OLGA	
JFE Engineering		Water-based scrubbing (B&W)	
Relax Umwelttechnik GmbH		Water-based scrubbing (B&W)	
Repotec		RME-based scrubbing	
Dahlman		Chlorine	Oil-based OLGA scrubbing (particularly dioxins)
ECN	Oil-based OLGA scrubbing (dioxins)		
Bayer	Sulphur	Catalytic removal	
Catalysts & Chem Ind. Co.		Catalytic removal	
Clearwater		Amine scrubber	
Comprimo		Hydrogenation, absorption, and adsorption	
DOW		Ammine scrubber	
Envirotherm		Dry and wet sulphur removal	
Gastec NV		Hydrogenation, absorption, and absorption	
Haldor Topsøe		Catalytic hydrogenation and absorption	
Johnson Matthey		Catalytic hydrogenation	
Linde		Methanol scrubbing (Rectisol)	
Lurgi		Methanol scrubbing (Rectisol)	
McDermott Technology Inc.		Regenerative adsorption	
Süd Chemie		Catalytic decomposition (COS)	
SulphCatch		Adsorption of organic compounds	
Texaco		Hydrogenation absorption, and adsorption	
Tokyo Gas		Regenerative zeolite ion based	
Uhde		Amine scrubber	
UOP		PE-glycol adsorption (Selexol)	
Air Liquide		NH ₃ and HCN	Water scrubbing
BASF			Catalytic conversion
Catalysts & Chem Ind. Co.	Catalytic conversion		
Dahlman	Water scrubbing		
Envirotherm	Catalytic reforming		

Company	Removal Technology	Detailed Information
HoSt		Water scrubbing
Linde		Amine-based scrubbing
Linde		Methanol-based scrubbing (Rectisol)
Lurgi		Methanol-based scrubbing (Rectisol)
Mitsubishi Heavy Industries		Water scrubbing
Paques		Biological (ANAMMOX)
Süd Chemie		Catalytic decomposition (particularly HCN)



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