An Outlook on Tar Abatement, Carbon Capture and its Utilization for a Clean Gasification Process

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https://doi.org/10.5109/4742115

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Abstract: The generation of syngas via gasification is accompanied by greenhouse gas emissions and certain impurities like tar. This is the major problem that makes the technology unattractive for commercialisation. Tar content present in the syngas limits its application as it causes damage to engines, while the CO_2 that accompanies it adds to the climate issues when released to the atmosphere. In this short review, an overview of techniques used for tar abatement, CO_2 capturing, and potential areas of CO_2 utilisation were discussed.

1. Introduction

Renewable energy, a clean environment, and a sustainable economy are the three major forces driving the global search for the alternative, replenishable, and lasting energy source [1, 2]. The rapid growth of the global population, industrialisation and rapid urbanisation has raised the energy requirement in the last century. Fossil fuel utilisation to catch up with this energy demand continuously generates problems of atmospheric pollution, global warming, ozone layer depletion and climate change, among others [3, 4]. Hence, it is noticed that increasing interest in the reduction of greenhouse gasses and fossil fuel usage has triggered research on renewable energy sources [5, 6]. Among these energy sources, biomass energy conversion seems to be the best as it is capable of supplying energy in solid form (bio char), liquid form (bio-oil), and gas (producer/ syngas) which are potential feedstock for the production of chemicals like methanol and ethanol [7, 8].

Biomass energy is that which is obtained from plants or plant materials. Biomass can be converted into fuel via thermochemical (combustion, pyrolysis, and gasification) and biochemical (fermentation, methanation and liquefaction) routes [9, 10]. Thermochemical conversion is more preferable to biochemical due to rapid conversion rate and a higher quantity of feedstock [11-12]. Biomass gasification simply means the thermochemical transformation of biomass to gaseous mixtures in the presence of a gasifying medium, which may be air, oxygen, or steam. The gaseous mixture comprises of methane (CH_4), carbon monoxide (CO), hydrogen gas (H_2) and carbon dioxide (CO_2), sulphur oxides (SOx) and alkaline gases and complex hydrocarbons [13-15]. The fuel can be utilised for producing chemicals and heat and power generation in internal combustion engines. Gasification gives the liberty of using individual feedstock or mixing different ones to achieve co-gasification [16].

Despite the wonderful products of biomass gasification (H_2, CO, and CH_4), the process is associated with some unwanted substances which have turned out to be arch-rivals of gasification [17]. These unwanted substances are the complex hydrocarbons commonly referred to as tar and carbon dioxide (CO_2), which accompany the producer gas, as illustrated in Fig.1. The tar and the CO_2 contents limit the usage of the syngas obtained, and they have made the gasification technology unattractive from a commercial perspective. Therefore, they are the significant problems of gasification that need to be addressed. The tar is formed at the pyrolysis stage during decomposition and therefore is released in the form of an aerosol, condensing to a sticky component. On the other hand, the CO_2 usually develops as a constituent of the gas stream (syngas) and therefore has to be captured. While the tar is responsible for various damages in the downstream usage like blockage and fouling in turbines and engines, cracking in filter-pores, low gasification efficiency and syngas calorific value, cocking, and

deactivation of catalyst [18], the CO_2 limits the efficiency of the syngas as it is a non-flammable gas. Both tar and CO_2 concurrently accompany the syngas during gasification, and therefore addressing the two issues simultaneously becomes imperative. Improved gasification systems incorporated with CO2 capture and sequestration mechanisms can fully store up to 90% of the CO_2 emitted from facilities that use biomass/fossil fuels to produce power, H_2 or syngas. Most importantly, such technologies are referred to as negative emissions technologies (NETs) and are essential contributors to curbing down CO_2 emissions from the environment [19]. New emerging technologies like the sorption enhanced gasification (SEG) process allow gasification and CO_2 capture simultaneously by applying a solid sorbent. SEG is therefore influenced mainly by sorbent properties (e.g. type and activity).

Depending on the gasifier type, the tar content ranges from 1 g/m^3 to 100 g/m^3. The produced tar results to lower gas yield, high maintenance and operation challenges such as corrosion, blocking and clogging of fuel pipes, filters, nozzles, and turbines [20-22]. Sasujit [13] argued that high tar

modification (separation of pyrolysis and reduction zones), optimised process conditions (temperature, gasification medium, pressure, additive/ catalyst, residence time and mass ratio between fuel and gasification medium). Hence this method limits or decreases the potential of tar formation during biomass gasification.

On the other hand, post-gasification abatement applies after the producer gas has been produced. Then, the tar is collected through physical processes involving cyclones, filters scrubbers, electrostatic precipitators or chemical treatment by catalytic and thermal processes and partial oxidation to purify the gas. Combining both methods is recommended for maximum tar removal with good quality product gas [23-25].

High greenhouse gas emissions such as CO_2 that accompanies the producer gas stream are harmful to the ecosystem [26, 27]. By implementing carbon capture, it can be handled as an essential raw material for the manufacture of several value-added fuels and chemicals, thus curbing emission problems, energy supply challenges, and multiplying the biomass fuel conversion yield. The idea of carbon capture, utilisation and sequestration
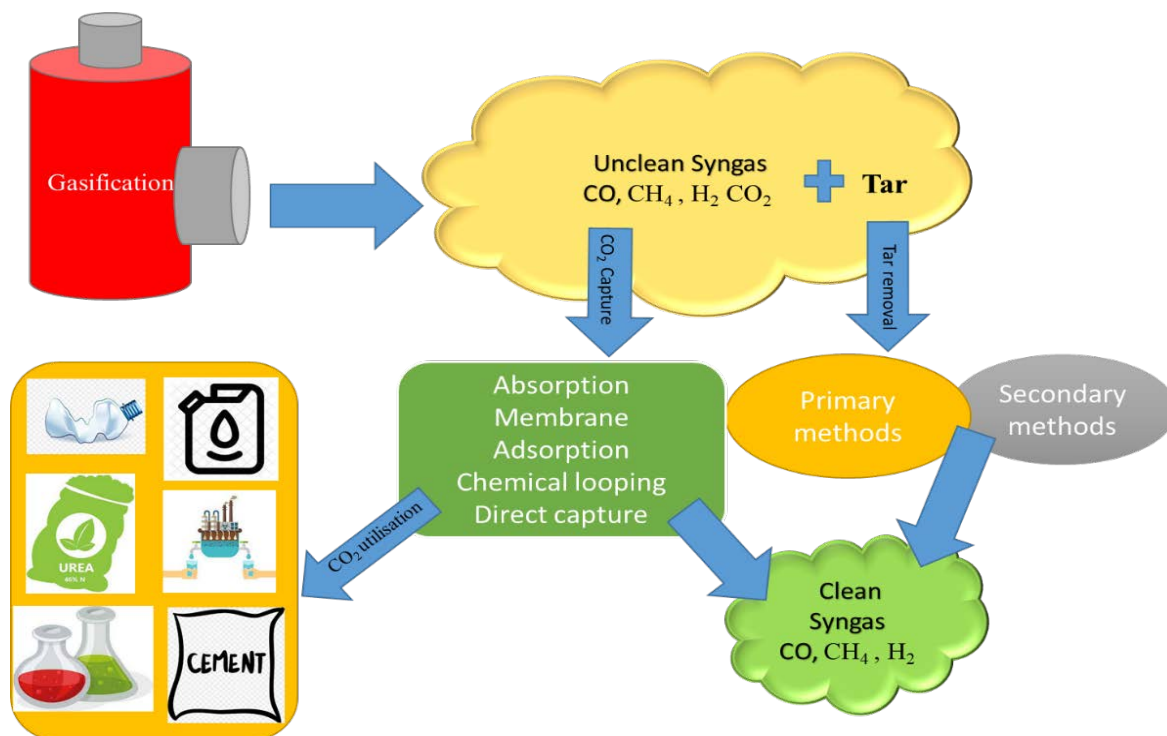

Figure 1. Schematic representation of CO_2 and tar removal during gasification

content discourages the implementation of the technology in high-efficiency IC engines and fuel cells where utmost priority is given to an extremely clean gas stream. The tar is a combination of different chemical compounds [11] as demonstrated in Fig. 2. There are numerous methods of tar abatement which are broadly classified into two: (1) Primary (in-situ) methods and (2) secondary (post-gasification) methods. In-situ reduction avoids tar formation, and is attained either by gasifier design

(CCUS) are concepts of CO_2 regulation and climate crisis. Carbon capture and storage (CCS) deals with the mechanism of selective ejection of CO_2 from producer gas streams, compressing it to a supercritical condition, after which it finally get transported and sequestered in exhausted oil and gas reservoirs and geologic formations [28,29]. The challenging fact with CCS is the high cost associated with capture and compression, which consumes about 75% of the entire cost of the CCS process,

and has highly impacted its large scale implementation. As a more promising and appealing substitute, carbon capture and utilisation technologies (CCU) have lately dominated the scene for the credit of transforming the captured CO_2 into a precious asset as a substitute for permanent sequestration. Styring et al. [30] argued that CCU manipulates captured CO_2 as a renewable energy resource to replace fossil fuel resources. Even though CCU is more advantageous than CCS, it is faced with the challenges of thermodynamic stability during the CO_2 conversion and utilisation in chemical reactions. CO_2 capture technologies are classified into two groups: (1) post-combustion which refers to direct CO_2 dismissal from flue streams and (2) pre-combustion which refers to using improved low carbon comprehensive combustion systems which involves an integrated gasification combined cycle (IGCC) and oxyfuel gasification (addition of uncontaminated oxygen to lower the CO_2 concentration of power generation) [28, 31].

This paper provides a short review of the most recent developments in carbon capture and tar abatements as methods that will purify producer gas stream obtained after biomass gasification. The concept has been demonstrated in Fig.1. The ultimate goal of producing syngas is to use it as fuel for power generation or feedstock for chemical synthesis. This may only be achieved through proper cleaning of the gas to remove the tar and capture the CO_2 [32, 33]. The paper gives an overview of the different pathways and the mechanisms involved in removing both tar and CO_2 according to past literature and further provides the potential application of the captured carbon. The paper is organised in the following order; section 1 introduction, section 2 biomass gasification, section 3 tar definition, formation, classification and reduction methods. Section 4 carbon capture separation techniques and utilisation of the captured CO_2, and lastly section 5 conclusion.

2. Biomass gasification

The term "gasification" refers to the thermochemical transformation of organic materials/solid fuels within a vessel referred to as the gasifier. This results in gaseous products commonly called producer gas. The producer gas is a mixture of gases such as carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and carbon dioxide (CO_2), volatile organic matter, water vapour, hydrogen sulphide (H_2S), tar, char, and ash [25, 34]. The reaction takes place within temperature ranges of 800-100 ºC, within a medium which may be air, oxygen, steam and flue gases [35, 36]. Details of gasification reactions are given in Table 1. The average calorific value of the producer gas obtained from biomass gasification ranges from 4-10MJ/m³, while the carbon conversion efficiency ranges from 50-70% [37]. The gasification process involves four stages as summarised below:

- Drying/Vaporisation stage: The earliest stage in gasification where excess water is removed from the feedstock, at temperature ranges of 70-200 ºC [38]. However, no thermal decomposition takes place in this zone as a result of low temperature [39].
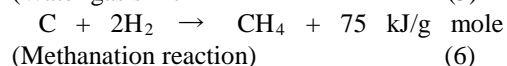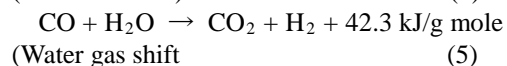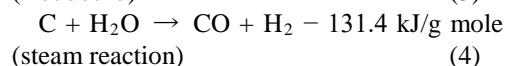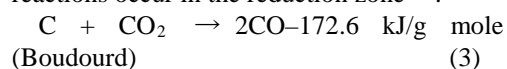Drying: Moist feedstock + Heat → Dry feedstock + water

- Devolatilization/pyrolysis: This stage occurs at a temperature of about 300-500 ºC, and involves the thermal breakdown of materials in an inert condition, which results in the emergence of liquid tar, solid char and gases, such as CO, CO_2, H_2, CH_4, H_2O, etc.
Pyrolysis: Dry feedstock + Heat → Char + Volatiles

- Combustion/ partial oxidation: Due to the presence of oxygen in this zone, the combustion reaction occurs with the volatile products and char obtained during pyrolysis. The reactions in this stage are highly exothermic in this zone and occur at a temperature greater than 500 ºC. Varying reactions occur between solid carbonized fuel and oxygen, resulting in carbon dioxide and a considerable amount of heat. Hydrogen also combines with oxygen to produce water vapours.

$$C + O_2 \rightarrow CO_2 + 406 \text{ kJ/g mole} \quad (1)$$
$$2H_2 + O_2 \rightarrow 2H_2O + 242 \text{ MJ/kg mole} \quad (2)$$
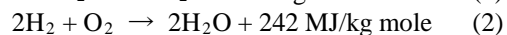
- Reduction/gasification: The char is converted into gases by reacting with hot gases coming from the oxidation zone at about 800 to 1000 ºC, resulting in the transformation of the sensible heat of the solid char and gases into the chemical energy of the producer gas. During this process, some combustible products are generated such as, CO, CH_4, and H_2. In addition, the following chemical reactions occur in the reduction zone [39]:

$$C + CO_2 \rightarrow 2CO - 172.6 \text{ kJ/g mole} \quad \text{(Boudourd)} \quad (3)$$
$$C + H_2O \rightarrow CO + H_2 - 131.4 \text{ kJ/g mole} \quad \text{(steam reaction)} \quad (4)$$
$$CO + H_2O \rightarrow CO_2 + H_2 + 42.3 \text{ kJ/g mole} \quad \text{(Water gas shift} \quad (5)$$
$$C + 2H_2 \rightarrow CH_4 + 75 \text{ kJ/g mole} \quad \text{(Methanation reaction)} \quad (6)$$
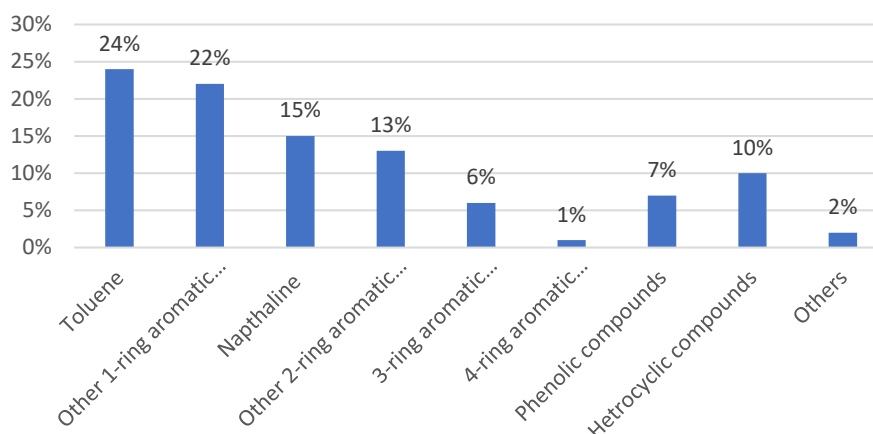
Figure 2. Typical composition of biomass tars [11)]

Table1. The gasification process reaction of ordinary biomass [40-42)]

Process reaction		Type of reaction
Volatile matter $= CH_4 + C$	Partially exothermic	Char oxidation
$C + \dfrac{1}{2}O_2 \rightarrow CO$	$\Delta H^* = -110.60\text{ kJ/mol}$	
$CO + O_2 \rightarrow CO_2$	$\Delta H^* = -393.60\text{ kJ/mol}$	
$CO + \dfrac{1}{2}O_2 \rightarrow CO_2$	$\Delta H^* = -283\text{ kJ/mol}$	Oxidation of volatiles
$H_2 + \dfrac{1}{2}O_2 \rightarrow H_2O$	$\Delta H^* = -241.90\text{ kJ/mol}$	
$C + CO_2 \rightarrow 2CO$	$\Delta H^* = 172.50\text{ kJ/mol}$	Boudourd
$C + H_2O \leftrightarrow CO + H_2$	$\Delta H^* = 131.30\text{ kJ/mol}$	Primary water gas
$C + 2H_2O \leftrightarrow CO_2 + 2H_2$	$\Delta H^* = 90.20\text{ kJ/mol}$	Secondary water gas
$C + 2H_2 \leftrightarrow CH_4$	$\Delta H^* = -74.90\text{ kJ/mol}$	Methane formation
$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	$\Delta H^* = -165\text{ kJ/mol}$	
$C + 3H_2 \leftrightarrow CH_4 + H_2O$	$\Delta H^* = -206\text{ kJ/mol}$	
$CO + H_2O \leftrightarrow CO_2 + H_2$	$\Delta H^* = -41.2\text{ kJ/mol}$	Water gas shift

Gasifiers are broadly grouped into three, namely, entrained flow, fixed bed, and fluidised bed gasifiers, subtypes exist and are given in Table 2. The classification is based on the arrangement of fuel and produced gas flow and the contact mode of fuel and gasification agent. In the fixed bed gasifier, there is intimate mixing between fuel particles and oxidising agents. The fuel travels naturally along the four stages (drying, pyrolysis, combustion, gasification) and makes a bed of solid fuel, over which the gasification agent moves freely. The fluidised bed fluidises the fuel with low-pressure gas or air, allowing more contact between the fuel and oxidiser for the reactions. The particle contact is low in entrained bed type, as the fuel particles are made smaller and fed through an atomiser to ensure maximum surface contact with the oxidisation agent. Further classification may be also due to the source of heating which may be allo-thermal that is externally sourced heating or auto-thermal if the source of heating is as a result of partial combustion of the fuel [24].

Table 2. Gasifier Types [24, 37, 43]

	Gasifier types	Gasifier sub-types	Gasification temperature °C	Suitable scale	Tar	Feed stock preparation
Gasification technologies	Fixed/ Moving bed	Downdraft	700-1200	Small-medium	Low	Very critical
		Updraft	700-900	Small-medium	High	critical
		Crossdraft	-	-	-	-
	Fluidised bed	Bubbling	< 900	Small-large	Medium	Less critical
		Circulating	1450	Medium-Large	Medium	Less critical
		Twin bed	-	-	-	-
	Entrained Flow	Coaxial down-flow	1450	Medium-large	Very low	Only fine particles
		Opposed jet	-	-	-	-

3. Tar

In the spring of 1998, a meeting was held in Brussels by the Energy Department of United States, the Directorate General of Energy of the European Commission (DG XVII) and the International Energy Agency (IEA) about tar quantification protocol, and was agreed that tar refers to all hydrocarbons whose molecular weight was greater than benzene (C_6H_6) [44]. Devi et al. [45] defined tar as a combination of condensable hydrocarbons, including aromatic compounds with up to five rings that may be oxygenated and Polycyclic Aromatic Hydrocarbons (PAHs).

3.1 Tar Formation, content and categorisation

Tar formation is initiated at the pyrolysis zone when the biomass fuel decomposes into char, liquid (primary) tar and volatiles at a temperature range between 200 to 500°C. Generally tar produced during producer gas condensation may be classified as primary, secondary and tertiary compounds. Primary tar is formed at temperatures below 500 °C, while at higher temperatures in the oxidation zone, the primary tar reforms to miniature molecules, non-condensable gases (CO, H_2O, CO_2) and larger molecules (secondary tar). At a later stage with a higher temperature about of 800 °C, the secondary tar decomposes completely and tertiary tar is produced [25]. Another classification of tar was developed by the Applied Scientific research center of Netherlands, Energy research center of Netherlands (ECN) and the University of Twente

Netherlands, based on solubility and condensability of different tar compounds. The two classifications, however, complement each other and are both critical [25]. The classification is presented in Table 3. Several researchers claimed lignin as the primary antecedent of tar as a result of its aromatic nature with the main components of its pyrolysis as vanillin (4-hydroxy-3-methoxybenzaldehyde, $C_8H_8O_3$), guaicol (2-methoxyphenol, $C_7H_8O_2$), catechol (1,2-dihydroxybenzene, $C_6H_6O_2$) and anisol (metoxibenzeno, C_7H_8O) [46-51]. However, Sasujit et al. claimed that tar composition depends on the temperature of the reaction, type of the reactor and the feedstock. For biomass tar, the main components are naphthalene, ethylbenzene, and acenaphthylene [13]. Feng et al. [52] used Gas Chromatography Mass Spectrometry (GC-MS) analysis to examine the evolution of tar during homogeneous conversion at temperature ranges between 500 and 900 °C . It was discovered that at temperatures below 600 °C, the highest proportion of the tar is composed of components based on the primary biomass tar consisting of oxygen and compounds like levoglucosan and dimethoxymethane. At temperatures greater than 700 °C, the transformation of the primary pyrolyzed tar takes place, and the composition becomes mainly made of aromatic compounds like naphthalene. Temperature addition led to the reduction or total tar removal containing branched compounds and the subsequent formation of PAHs. Some tar components break down into more minor molecular gases and C1~C5 hydrocarbons. As the temperature reaches 900 °C, PAH constituents like naphthalene, phenanthrene, and anthracene increased, leading to the evolution of more stable aromatic hydrocarbons.

Table 3. Classification of tar compound [53]

Tar class	Class name	Property	Representative compounds
1	GC-undectable tar	Extremely large tar compounds, not visible under a GC-FID or GC-MS equipped with a non-polar capillary column	Obtained by subtracting the gas chromatography-detectable tar fraction from the total gravimetric tar
2	Heterocyclic	Tars containing heteroatoms; highly water-soluble compounds	Pyridine, phenol, cresols, quinolone, dibenzophenol
3	Light aromatic (1 ring)	Usually light hydrocarbons with a single ring; do not pose a problem regarding condensability and solubility	Toluene, ethylbenzene,xylenes,styrene
4	Light PAHs compounds (2-3) rings	2 and 3 ring compounds; condense at low temperature even at very low concentration	Indene, naphthalene, methylnaphalene, biphenyl, acenaphthalene, fluorine, phenanthrene, anthracene
5	Heavy PAHs compound (4-7 rings)	Compound larger than 3 rings, these components condense at high temperatures	Fluoranthene, perylene, pyrene, coronene, chrysene

3.2 Tar reduction

Effective use of producer gas in different applications such as gas turbines, internal combustion engines, fuel cells, methanol, and ammonia synthesis depends on its tar level. Therefore, the acceptable limit of tar level is

recommended to be between 50-100 mg/Nm^3. Tar limits for various applications is given in Table 4. Hence it becomes imperative to bring down the level of tar within producer gas to enable its use for multiple applications. As mentioned earlier, there are two methods of tar reduction: the in-situ (primary) method and the post-gasification (secondary) method.

3.2.1 In- situ (primary) methods

In-situ methods refer to precautions implemented during the gasification stage to completely avoid tar formation or break down the tar formed in the gasifier. This is possible through the adoption of proper operating conditions and gasifier design.

3.2.1.1 Operating conditions

Important operating conditions such as temperature, pressure, residence time, gasification medium, catalyst/ additives and mass ratio between fuel and gasification medium play a vital role in the resulting gasification quality. These factors affect the syngas quality, tar formation and carbon conversion efficiency [45]. The gasification temperature and pressure play a significant role in the reduction of tar as it enhances cracking. Several studies have depicted that with an increase in temperature, the levels of tar in producer gas decrease. Chan et al. gasified sawdust in air and increased the temperature from 780-857 ºC, and the tar produced dropped from 2.0-0.3 g/Nm^3 [54]. The same scenario is also valid on the effect of pressure, as the more the gasification pressure, the less the tar. Tuomi et al. [55] demonstrated the impact of pressure on tar decomposition activity of different catalysts. As the pressure was increased from 1-10 bar, the catalytic activity for olivine and sand increased thereby increasing tar conversion. The gasification medium, which may be air, steam or oxygen, affects the production of tar. Rios et al. [25] reported that more tar is produced when steam is used while less is obtained when air is used. This may be due to the lowering of the temperature by steam injection. Air fuel ratio also influences tar production. When air is used as the gasification medium, the parameter is referred to as the equivalent ratio. It is reported that with increased ER, tar content decreases as a result of more oxygen availability to break the volatile compounds in the pyrolysis zone. In terms of residence time, Rios et al. [25] further reported that with longer residence time, 1 and 2 aromatic ring compounds decreased significantly, resulting from long exposure of tar compounds to oxidising medium, resulting in a 75% of tar reduction. Catalyst also plays a significant role in tar removal and have proven to be effective. Catalytic cracking can transform tar to low molecular weight hydrocarbons and valuable gas products (H_2 and CO). According to Islam [18], tar abatement is best achieved through the use of catalyst, and these catalysts have been characterised with the following properties;

- It is necessary that the catalyst must be efficient

for tar reduction in a gas stream having maximum amounts of H_2, CO, CO_2, and H_2O within temperature limits of 600 °C–900 °C.

- If syngas is the target output, then the catalyst should be capable of methane reforming
- The catalysts should provide a suitable syngas ratio (H_2/CO) for the intended process.
- The catalysts should withstand deactivation in the event of carbon fouling, sintering, and poisoning.
- It should be simple to regenerate the catalyst.
- The catalysts should be attrition resistant.
- The catalysts should be affordable and easily accessible.
- It should not be environmentally hazardous.
- The catalyst should be resistant to sulfur poisoning.

Table 4. Permissible tar levels in producer gas for different applications [25]

Application	Tar Limit (mg/Nm^3)
Direct combustion	No defined limit
Internal combustion engine	<100
Gas turbine	<5.0
Synthesis of methanol	<0.1
Compressors	50-500
Fuel cells	<1.0
Fischer Tropsch synthesis	<1.0 µL/L (class 2,BTX)

3.2.1.2 Gasifier design

The type of gasifier and its design affects the level of tar in a producer gas [56]. This might be a result of the gasifier configuration. In the updraft gasifier, the produced gas with a mixture of tar escapes from the top of the gasifier. And as a result of heat exchange with cooler surfaces of the gasifier, conversion of the primary tar to secondary tar and gases becomes minimal. This results in producer gas with a high tar content of about 50 g/Nm^3. In downdraft gasifiers, the produced gas passes through the bottom of the gasifier along with built tar. In so doing, the primary tar passes through the combustion zone. The high temperature and sufficient oxygen present in that zone enable tar to crack into condensable gases. This results in producer gas with a less tar content <20 g/Nm^3. When fluidised bed gasifiers are used, lower tar content is recorded due to the high level of mixing between the bed material and fuel. This results in high biomass conversion to gases with minimum tar. For bubbling and circulating fluidised bed, tar content ranges from 5-20 g/Nm^3 and 1-5 g/Nm^3, respectively. In an entrained flow gasifier, the tar level is very low as the produced tar passes through a very high-temperature region > 1000 ºC. The separation of the

gasifier zones results in a multistage process that is different zones of drying, pyrolysis, reduction and gasification. This leads to increased efficiency of the process with qualitative producer gas [25]. An effective reduction in tar level of about 10 mg/Nm^3 has been reported by Cao et al. [57,] and this was achieved by developing a lab-scale combined 2-region reactor gasifier. Galindo et al. [58] also conducted a similar study where tar level was brought down by introducing air in 2-stage gasification, which triggered the temperature within the reactor. Hence this influenced thermal tar cracking, thereby lowering 87% of tar content in the syngas. Some gasification systems feature separate zones of drying, pyrolysis, gasification and combustion, and the multiple stage process has been found to reduce the amount of tar. Xiao et al. [59] constructed a dual-chamber Internally Circulating Fluidized Bed Gasifier (ICFG) having separate functions for gasification and combustion with bed material circulating between two chambers. The resulting syngas had minimum tar. A similar low tar result was also reported by Burhenne et al.[60] where a fixed bed gasifier with four different zones was used for syngas production

3.2.2 Post-gasification (secondary method)

Post-gasification methods are applied after the completion of the gasification process, and product gas has been collected. The process of removing tar from the gas may be a through physical process or partial oxidation, thermal and plasma cracking.

3.2.2.1 Physical/ mechanical process

The physical cleaning methods collect the tar in a condensed form and are divided into two depending on the temperature of the gas. The dry gas cleaning method is employed at a temperature range of 200-500 ºC or 600-800 ºC. However, it is advisable to cool the gas when using fabric filters as elevated temperatures affect the resistance of bag material fabric [61]. Equipment used for dry cleaning includes cyclonic separators, electrostatic precipitators, ceramic filters, bag filters, and catalytic filters. The wet gas cleaning is conducted at a temperature range of 20-60 ºC when the gas temperature cools down. Equipment used for wet cleaning includes the spray towers scrubbers, impingement, wet cyclone, venturi scrubbers and wet electrostatic precipitators. A combination of dry and wet methods has also been developed, referred to as the OLGA method [62]. The OLGA technique removes and reuses valuable tar components with minimum operational cost. Its operating temperature lies in the range of 60- 450 ºC. Oil is utilised as the absorbent medium instead of water. Like water scrubbing, tars classified as 1, 4, and 5 are regenerated by condensation as the temperature is lowered below the tar dew point. Lighter tar compounds classified as 2 and 3 are subsequently removed via absorption into a second liquid scrub. Compared to conventional dry and wet procedures,

the OLGA process brings numerous benefits. In addition to eliminating waste treatment, this strategy overcomes the technical and financial challenges of catalytic and high-temperature tar removal. Highly poisonous PAHs are always an issue; however, these tars are usually easier to extract from the water because of their volatility and limited water solubility. The main problem is highly soluble tar and phenol in particular. They easily dissolve in water hence challenging to remove. The removal of these tars using oil prevents costly wastewater treatment. The oil may then be regenerated simply or utilized as a feedstock [25].

3.2.2.2 Thermal oxidation plasma and thermal cracking

The outlined methods are only applied to reactors with high-temperature zone 900-1300 ºC. Partial oxidation is achieved through the addition of air or O_2 in oxidation reactors. It proves to be an effective way of tar removal when it is conducted at a very high temperature. In a study by Zheng et al., partial oxidation was performed between 600 to 1400 ºC, and the results indicated tar reduction with temperature increase [63]. Lately, plasma, the fourth state of matter consisting of excited atoms and molecules, a mixture of ions, radicals, neutral particles, is now used for tar reduction [13]. It is classified into two; thermal and non-thermal plasma. For thermal plasma-like gliding arc discharge and arc discharge, the gas temperature exceeds 1730 ºC. In the case of non-thermal plasma, such as corona discharge/ and dielectric discharge, the electrons temperature may get up to 104-105 ºC while the gas temperature may be the same as that of the surrounding. High tar abatement efficiency could be achieved by implementing plasma technique despite some drawbacks like high cost, having a limited lifetime for pulse power supplies and a high energy requirement from the overall process. When a catalyst is incorporated in a plasma reactor, there seems to be a synergy that leads to increased tar conversion into valuable energy and syngas products. This is because catalysts can enhance water gas shift and steam reforming reactions that stimulate the production of H2 and CO. Hence, a synergistic effect is likely to result through a combination of non-thermal plasma with a catalyst [25].

4. Carbon capture

A sufficient amount of carbon dioxide is generated during thermochemical processes like gasification and combustion of natural gas, which is either released to the atmosphere or utilised in manufacturing plants or food processing industries [64]. Likewise, in the case of thermochemical processes, especially biomass gasification, a considerable amount of CO_2 (about 20%) is released, and most of it goes back to the atmosphere. Quite a number of methods, either chemical or physical, have been applied to control CO_2 emission in gasification

and combustion processes [65]. Amongst these methods, two chemical techniques have been proven to be the best and most conventional in terms of gasification and combustion processes owing to their high efficiency. These are the calcium looping method that results in a low CO_2 gas stream [66] and chemical absorption via monoethanolamine (MEA), widely used as a commercial method on an industrial scale [67]. In addition to capturing the CO_2 for storage in geological formations, its utilisation will influence the commercialisation of the biomass thermochemical conversion processes [68]. This can be achieved by compressing the CO_2 to a dense fluid (liquid state) and transporting it via pipelines, leading to an underground storage facility (geological formations).

4.1 Carbon capture separation techniques

4.1.1 Absorption

Absorption based CO_2 removal is performed by the application of physical or chemical solvents. Chemical solvents like aqueous ammonia, amine-based solvents such as monoethanolamine (MEA), diethanolamine (DEA), and N-methyldiethanolamine (MDEA) and alkaline solvents such as $Ca(OH)_2$ and NaOH, are used in post-combustion capture [28]. This post-combustion capture is achieved via the stripping process, where CO_2 and the chemical solvent (saturated) are introduced to heat, producing a new solvent and releasing the CO_2 at the tip of the stripping chamber [64]. In the physical methods for CO_2 capture, the gas is made to come in contact with the solvent stream, and the CO_2 is being captured by the solvent physically. The physical methods have been well-established not long ago and include Selexol, Rectixol, Purisol, and Fluor. Lately, ionic liquids have been recognised as potential physical solvents due to their properties, including elevated thermal stability at high temperatures, low volatility, low vapour pressure, and low energy requirements. However, the main hindrance to their utilisation is their low working capacity. The challenge facing the absorption technology is that high energy is required for solvent regeneration. Other challenges include corrosion and a large volume of water requirement. It is recommended that solvents with a high heat of absorption ($>60 \, kJ \, mol^{-1}$) may reduce energy consumption while utilisation of thermally stable solvents with low regeneration energy requirements can significantly improve the thermodynamic efficiency of the separation process. Additionally, impurities in the gas streams quickly deteriorate the chemical solvents; therefore, high tolerant solvents should be considered in such applications [28].
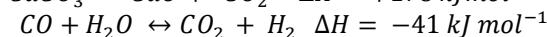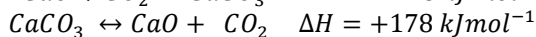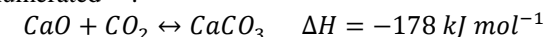
4.1.2 Membrane

Membrane separation is established on the Knudsen diffusion principle and occurs under steady state conditions with pressure difference across the membrane driving the permeation process. The separation performance of a membrane is influenced by its structure, morphology, make-up and operating conditions. Membrane separation is more suitable for high-pressure pre-combustion techniques such as IGCC, and less ideal for low-pressure post-combustion applications. Different membrane types exist, including the porous inorganic membrane composed of zeolites, metal organic frameworks (MOFs), carbon molecular sieves (CMS), ceramics, and a few oxides. Inorganic membranes can endure elevated temperatures and have high mechanical stability, but their high cost lowers the chances of commercialisation. Their main limiting factor to their industrial scale usage is their long term stability, reliability and fabrication route, which is very expensive. There is also the polymeric membrane which has a high potential for industrial usage with a high packing density greater than that of inorganic membranes. However, some of their disadvantages in CO_2 capture include low separation performance, low CO_2/N_2 selectivity and permeability for post-combustion processes, a limited imbalance between permeability and selectivity, swelling, deterioration, reactive to impurities, and mechanical stability, especially for high-pressure operations. Facilitated-transport membranes (liquid membrane, ion exchange membrane) are also recommended for CO_2 capture. However, their drawbacks include contamination by SOx and NOx and long term stability. The mixed matrix membrane originates from dispersed highly selective molecular-sieve particles such as zeolites and carbon nanotubes in a polymer matrix. They are currently at the initial stage of development and are very expensive and complex to manufacture [69].

4.1.3 Adsorption

Adsorbents are porous solid materials used to remove CO_2 from gas streams and are classified into high temperature and low temperature materials. The high temperature materials are all chemisorbents, including hydrotalcites, alkali/alkaline earth oxides like calcium oxides, alkali silicates, and double salts. Low temperature adsorbents are physisorbents like carbon based materials such as graphene, carbon nanotubes, carbon nanofibres, porous polymer networks, molecular sieves, and covalent organic frameworks. It is desirable that adsorbents are cheap, have a high working capacity, low regeneration requirement, stability and rapid kinetics. Also, for optimum efficiency of the process, factors like cycle time, pressure, temperature and bed quantity, cycle configuration and a number of steps and number of the bed are among the important parameters to be into account for effective capture [28, 70, 71]. One of the recent upcoming technologies as mentioned earlier is the SEG in which the use of limestone especially $CaCO_3$ has been applied due its ability to capture carbon in gas stream during gasification. Optimisation of the CO_2 capture in the gasifier and the release of CO_2 in the combustor, requires operation of the reactors at particular temperature settings as defined by the $CaO/CaCO_3$ equilibrium. Major

chemical reactions that take place during SEG process are enumerated [19]:

$$CaO + CO_2 \leftrightarrow CaCO_3 \quad \Delta H = -178 \, kJ \, mol^{-1}$$
$$CaCO_3 \leftrightarrow CaO + CO_2 \quad \Delta H = +178 \, kJ mol^{-1}$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41 \, kJ \, mol^{-1}$$

The effectiveness and cost of the adsorption process depend on adsorption processes like pressure/temperature swing adsorption, which are determined by the properties of the adsorbents, with process design and operation factors. For successful gas separation in industrial applications, adsorbents are required to be cheap, possess quick regeneration ability, adequate stability, capability and selectivity, low cost, low regeneration requirements, and high reactivity. Process parameters for maximum capture include cycle setting and duration, amount of steps and beds, and operation conditions (pressures and temperatures). Almamoori [28] related that adsorption-CO_2 capture could overcome most of the difficulties faced by absorption processes. However, the currently established technologies are not economically feasible at their present developmental stage. Industrial scale operation is yet to be fully implemented. In designing, developing and evaluating high-performance adsorbents, realistic performance and process considerations should be given priority.

4.1.4 Chemical looping

Chemical looping allows the separation of CO_2 and H_2O from the gas stream. It also aids in minimising NOx emission. Chemical looping is combined with IGCC in the case of pre-combustion capture to produce syngas. The technique utilises a metal oxide as an oxygen driver between the air and fuel reactors. Hence in the case of an extensive application, the availability of suitable oxygen drivers with high reactivity in terms of oxidation and reduction, stability, resistance to agglomeration, and the high melting point seem to be challenges of the chemical looping process. Oxides of transition metal-like calcium (Ca), iron (Fe), copper (Cu), cobalt (Co), molybdenum (Mo), manganese (Mn), chromium (Cr), niobium (Nb), vanadium (V), cerium (Ce) and indium (In) are mainly employed for chemical looping. These transition metals used in this process are expected to withstand agglomeration and high temperatures, possess high oxidation/reduction activity, are mechanically stable, and should be economically and environmentally friendly. On the other hand, the challenge of this system is the high-pressure requirement to attain maximum efficiency, and most of the chemical looping technologies to be applied for power generation are still at the lab scale under investigation [70].

4.1.5 Direct CO_2 capture from the atmosphere

When CO_2 is removed directly from the atmosphere or ambient air, it is called direct capture (DAC). It has recently become an attractive technology as it avoids the need to transport captured CO_2 from emitter site to sequestration sites. If widely adopted, it can reduce the overall CO_2 level in the atmosphere. The technology is quite similar to adsorption-based capture but has the challenge of material requirement with strong binding affinities and high CO_2/N_2 selectivity. Several materials like NaOH, CaOH, potassium solutions and solid materials, including alkali and alkali-supported carbonates, anaionic-exchange resins, amine functionalised metal oxides and MOFs have been evaluated for DAC [72].

4.1.6 CO_2 captured by hybrid process

Hybrid CO_2 capture, as the name implies, combines two capture subsystems or more simultaneously. The hybrid technology combines two or more separation units in series or parallels to simultaneously optimise the separation efficiency and lower the cost of the separation. An example of such a hybrid system is that developed by American Air Liquide where the CO_2 capture is done through the hybrid membrane-cryogenic distillation process [28]. Also, hybrid concepts of membrane-pressure swing adsorption and membrane-distillation have been investigated. The hybrid capture may be considered to deliver novel methods that will be effective and economically viable. Researchers must focus on feasibility, economic viability, material availability, environmental concerns and process conditions [73].

Most of the capture methods highlighted are still at the development stage and have not yet reached industrial scale. Thus engineers and material scientists have to work together on the material properties and process performance to develop feasible, cost-effective and functional CO_2 mechanisms. Some of the prospects and challenges of the capture techniques are highlighted in Table 5.

4.2 Captured CO_2 utilisation

The transformation of the captured carbon into valuable products is a very attractive way of embarking on the carbon capture culture, rather than releasing it freely into the atmosphere. To ensure sustainability, the process has to be eco-friendly safe and affordable. Table 6 highlights the opportunities and challenges rendered by the various CO_2 utilisation technologies.

Table 5. Prospects and Challenges of CO_2 capture methods [28]

Capture Method	Prospects	Challenges
Absorption	Ionic liquids and advanced amines utilisation, improved commercially available technology for absorption	Equipment deterioration, amine degradation, increased energy consequences, effect on the environment, high restoration energy
Membrane	Mixed-matrix membranes, composite hollow-fiber membranes, hybrid membrane–cryogenic processes	Does not suit high temperature applications, high energy required for post-combustion application, expensive to fabricate novel membranes, low selectivity, trade-off between purity and recovery
Adsorption	Structured adsorbents, composite adsorbents, rapid swing cycles, hybrid membrane- pressure swing adsorption	Heat control, adsorbent wear and pressure drop, prolong compatibility to moisture and impurities
Chemical looping	Changes to process design, composite oxides as O_2 conveyors	Reliable O_2 conveyor materials, pressurised operation
Direct capture	Structured adsorbents, direct air capture with renewable energy resources	Extremely dilute CO_2, high energy requirement, manufacture of robust materials
Hybrid capture	Membrane distillation, pressure–temperature swing adsorption process, membrane pressure swing adsorption	Not well researched, hybrid materials production, improvement of synergy and process upgrade

Table 6. Challenges and opportunities of CO_2 utilisation technologies [30]

Utilisation technology	Chemical conversion	Enhanced oil/gas recovery	Mineralisation	Desalination
Challenges	Complexity of reaction pathways High operation conditions Stability of catalyst to coke formation Development of highly selective catalyst	Transportation of CO_2 Large number of parameters involved Fluctuations in oil price	Slow kinetics High pressure and high temperature operation Expensive to implement	Equipment corrosion Expensive operation Large amount of brine
Opportunities	Dry reforming of methane Catalytic reduction to formic acid and its derivatives Noble-metal-doped transition-metal catalyst Biological pathways to synthetic fuels Oxidative dehydrogenation	Water alternating gas system (WAG) Compensated Neutron log (CNL)	Indirect carbonation Utilisation of inorganic wastes	Providing potable water to residential and municipal customers Possible implementation in various regions Modified Solvay process

Al mamoori et al [28], enumerates the primary applications of the captured CO_2 as in:

- Enhanced oil and gas recovery
- Chemical conversion
- Mineralisation
- Desalination

Also, the US Department of Energy categorised captured carbon utilisation techniques into four main areas that the CCS program supports:

- Cement industry
- Polycarbonate plastics
- Mineralisation
- Enhanced hydrocarbon recovery

Broadly, CO_2 is used as a raw material in food industries for preservation, urea production, water treatment, enhanced oil and gas recovery, in chemical production and polymer synthesis with a current global usage of 232MT-1.

Recently, less than 1% of released CO_2 into the atmosphere is being utilised in the mentioned industries [74]. In the enhanced oil and gas recovery (EOG/EOR), CO_2 is introduced into an oil reservoir where it combines with trapped oil in the rock formation. The CO_2 together with the oil is then pumped out of the rock where the former is separated and re-injected back to repeat the process, and the oil is collected. Melza et al. [75] claims this process to be more efficient than the conventional oil recovery technique, as the oil, on mixing with CO_2, expands and becomes lighter and easier to recover. CO_2 has the potential of partially replacing fossil fuels as its conversion into fuels seems to be the best way in CO_2 utilisation. CO_2 can be used in the synthesis of fuels such as methanol, methane, syngas, and alkanes, and such fuels may be used in power plants, transportation and fuel cells. Furthermore, CO_2 is used as feedstock in chemical production, most notably in the production of urea (160 Mt year-1), polyurethane (18 Mt year-1), inorganic carbonates (60 Mt year-1), acrylic acid and acrylates (10 Mt year-1), polycarbonates (4 Mt year-1), and alkene carbonates (a few kt year-1) [28, 76]. Urea, a major fertilizer, possesses the highest market for CO2 utilisation and is also used for fine chemicals, polymer synthesis, pharmaceuticals, and inorganic chemicals [77]. In the area of mineralisation, CO_2 is treated with metal oxides like magnesium and calcium oxides that naturally exist as mineral silicates. This is done by increasing the temperature and injecting fluids that have high a concentration of CO_2, thereby enhancing the carbonation kinetics [78]. Captured CO_2 is also utilised in removing total dissolved solids (TDS), thereby converting brine to pure water. Though the technique is efficient, but the main barrier towards its implementation is a cost implication. Also, CO_2 if exposed to sea water mixed with ammonia forms weak bonds, resulting in the removal of ions from the water phase. These compounds are formed NA_2CO_2 and NH_4Cl, and due to their weight, they settle at the bottom of the tank [79], while the fresh water is collected

for other uses.

4.2 Conclusion

Tar removal and carbon capture techniques have been reviewed and shown to be effective in purifying gas streams. Even though some of the tar removal techniques have been applied to biomass gasification process, most of the CO_2 capture and utilisation techniques are yet to be applied. This may be due to the CCU techniques are still being at the laboratory stage of development. Combined CO_2 capture and utilisation will lead to smaller, cleaner and more energy efficient technologies. This will ensure the production of clean gas while mitigating the release of CO_2 into the atmosphere, as the captured carbon will be utilised for value-added products. Despite the promising prospect of this approach, challenges like that of cost implication, thermodynamic instability of the captured CO_2, technology scale-up, technology efficiency, and implementation risk currently limits its practical use. Full commercialisation of biomass gasification may be attractive to investors if a gasification system that incorporates both tar abatement and carbon capture systems may be developed. However, such studies are scarce in biomass gasification, even though some modelling studies on the aspect of carbon capture have been reported. Future research should focus on the design of systems, with integrated tar and CO_2 capture units, as part of the producer gas conditioning (cooling and cleaning) system that will be financially viable. According to the review, efficient methods recommended can be incorporated, that is insitu and post gasification methods for tar abatement and calcium looping and chemical absorption via monoethanolamine for carbon capture. Biomass gasification has a lot of prospects in the near future where green fuels will take over the fossil fuel market. Hence there is need for developing a system that produces clean fuel free of tar and CO_2 gas that could be used directly. This calls for collaboration between engineers and material scientists to come up with viable techniques through the use of sustainable materials and catalyst. This will go a long way in achieving cleaner syngas and commercialising the gasification process.

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