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A critical review and technological outlooks**

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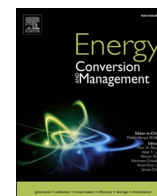
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Review

Biomass chemical looping gasification for high-quality syngas: A critical review and technological outlooks

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ABSTRACT

Biomass chemical looping gasification (BCLG) offers significant advantages over the conventional biomass gasification process in terms of enhanced gasification efficiency, inherent CO₂ capture, process circularity, and mitigated emissions of pollutants. This review discusses the prevailing status of research and development of BCLG in terms of production of high-quality syngas and negative carbon emissions based on the latest experimental and modelling studies. In particular, the design of the BCLG process and reactors is compared with conventional gasification. This review suggests that the BCLG process could be 10–25 % more efficient than the conventional combustion and gasification system in terms of economical H₂-production cost (3.37 USD/kg H₂-produced) and negative life cycle emissions of CO₂ (−14.58 kg-CO₂e/ kg-H₂ produced). This review has extensively considered the effects of process parameters and oxygen carriers (OCs) on gasification chemistry and reaction engineering during BCLG experiments. More specifically, the properties of OCs have been holistically analysed from technological, economic, and environmental perspectives to screen appropriate and affordable OCs for BCLG. In addition, the state-of-the-art modelling studies on BCLG are compared in terms of thermodynamic equilibrium, kinetics, and integrated processes. Technological challenges and research gaps in experiments and modelling have been highlighted in order to advance the BCLG process for industrial applications. In particular, further experimental work is needed to tackle issues related to stability and deactivation of OCs, fluidisation and circulation, the mechanical strength of OCs, the optimisation of feed conversion, and the integration and management of various thermal reactors. It is also desired to enhance the accuracy of models by incorporating optimisation of integrated processes and a more detailed reaction mechanism. Overall, BCLG is a promising negative emissions technology for renewable energy production, yet more innovative efforts in experimental and modelling studies are imperative to move towards more practical applications.

1. Introduction

In recent decades, as more countries are becoming industrialised, the world is witnessing a massive growth in energy demand, which has

accelerated the exhaustion of fossil fuels. Globally there is a consensus that the combustion of fossil fuels is the most significant contributor to increased CO₂ emissions leading to global warming [1]. Therefore, tremendous efforts are seen to rapidly reduce our reliance on fossil fuels

Abbreviations: TES, Total Energy Supply; ASU, Air Separation Unit; BCLG, Biomass Chemical Looping Gasification; BECCS, Biomass Energy Integrated with Carbon Capture and Storage; BIGCC, Biomass-based Integrated Gasification Combined Cycle; BIGCC, Biomass-based integrated gasification combined cycle; BM, Bed Material; CCE, Carbon Conversion Efficiency; CCS, Carbon Capture and Storage; CFBG, Circulating Fluidized Bed Gasification; CG, Conventional gasification; CGE, Cold Gas Efficiency; CGPO, Conventional gasification with pure oxygen; CLP, Chemical Looping Process; CRM, Chemical Reaction Model; DAEM, Distributed Activated Energy Model; HM, Homogenous Model; LHV, Lower Heating Value; OC, Oxygen carrier; OTC, Oxygen Transport Capacity; PL, Poultry; PW, Pinewood; RBRN, Phase Boundary Reaction Model; RDX, Energy-dispersive X-ray; RH, Rice Husk; RNSGM, Random Nucleation and Subsequent Growth Model; RS, Rice Straw; SBR, Steam to Biomass Ratio; SCM, Shrinking Core Model; SEM, Scanning Electron Microscopy; SMR, Steam Methane Reforming; SS, Sewage Sludge; TEM, Thermodynamic Equilibrium Modelling; TGA, Thermogravimetric Analysis; TPO, Temperature Programmed Oxidation; TPR, Temperature Programmed Reduction; TRL, Technology Readiness Level; WaS, Walnut Shell; WS, Wheat Straw; XRF, X-ray Fluorescence.

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and ramp up renewable energy capacities. However, since 2018, the share of renewable energy sources including solar PV, solar thermal, hydro, wind, biofuels, renewable municipal waste, tidal and geothermal in Total Energy Supply (TES) was just 13.5 % [2]. Among these mentioned renewable sources, energy from biomass forms a significant share, contributing 9 % to the TES. Therefore, biomass, one of the oldest energy vectors, will continue to play a pivotal role in reaching climate goals.

Biomass holds a long history as one of the essential energy sources, as it is abundantly available with a global production of about 60 EJ per annum [3]. Biomass will replace approximately 30 % of the United States petroleum consumption by 2030 [4]. In addition, the EU recently adopted a goal of 32 % renewable energy by 2030 in which energy from biomass will play a key role. Generally, biofuels are considered a carbon-neutral resource because the CO₂ emitted during biofuel combustion can be removed from the atmosphere and stored in the biomass during the photosynthesis process [5]. However, a critical review suggested that the bioenergy carbon-neutrality argument depends on a consideration of the time period consideration, emphasising the maximisation of either short-term or long-term climate benefits [6]. Additionally, we can ascribe a small carbon footprint to this method when considering production, transportation, and usage. Nevertheless, the overall carbon footprint becomes negative when we consider carbon capture and storage (CCS) [7].

IPCC in their fifth assessment report highlighted the significant contribution that biomass energy integrated with carbon capture and storage (BECCS) could make to the attainment of ambitious climate goals [8]. In line with this, a detailed comparison was made of seven carbon removal technologies, including BECCS, direct air capture and storage, biochar and soil carbon sequestration, afforestation and reforestation, ocean fertilisation, and enhanced weathering [9]. Among the options considered, the investigation identified BECCS as most suitable, with a carbon removal potential of 0.5–5 Gt CO₂ per annum and a removal cost between 100 and 200 US\$ per ton of CO₂. In Europe, the Energy Technology Institute assessed 28 different BECCS technologies, including the chemical looping process (CLP) [10]. The study concluded that CLP is a highly competitive technology with the lowest cost for CO₂ reduction. Similarly, in their energy roadmap report the US Department of Energy concluded that CLP provides the best cost reduction benefit among the available CCS technologies [11]. Interestingly, a techno-economic and environmental impact study comparing 12 different hydrogen production technologies showed that biomass gasification with CCS has the lowest life CO₂ emissions (−14.58 kg-CO₂e/ kg-H₂ production) with a levelised cost of 3.37 USD/ kg-H₂ produced and a TRL of 3–5 (see Fig. 1) [12]. Overall, there is an increasing agreement that CCS will be necessary to stabilise the atmospheric CO₂ concentration, and CLPs have emerged as one of the most cost-effective pathways.

CLP is based on the concept of splitting a conventional reaction into two or more sub-reactions by utilising the redox cycle of a solid looping material [13]. Typically, an overall reaction is divided into two sub-reactions that occur in separate reactors. For example, a looping material that generally is an oxygen carrier (OC) is reduced in one reactor followed by regeneration (or reoxidation) in another reactor, thus forming a closed loop between the two interlinked reactors [1]. The material is composed of a metal oxide that acts as an OC and/or an inert material. Compared with other CCS technologies, the main advantage of the process is the higher efficiency, minimised exergy loss, reduced energy penalty, and simplified product separation [1,13,14].

The basic idea for CLP can be traced back to the concept of the H₂ production process using steam-iron reforming and the production of syngas and CO₂ in the 19 century [3,15]. Nevertheless, the term 'chemical looping' was first coined by Ishida et al. [14] in 1987, wherein the authors used metal oxide as OCs for oxidation–reduction cycles in a combustion process. Despite the attractive features and advantages of CLP, it could not be realised on a fully commercial scale due to technological challenges, which are mostly related to the performance of

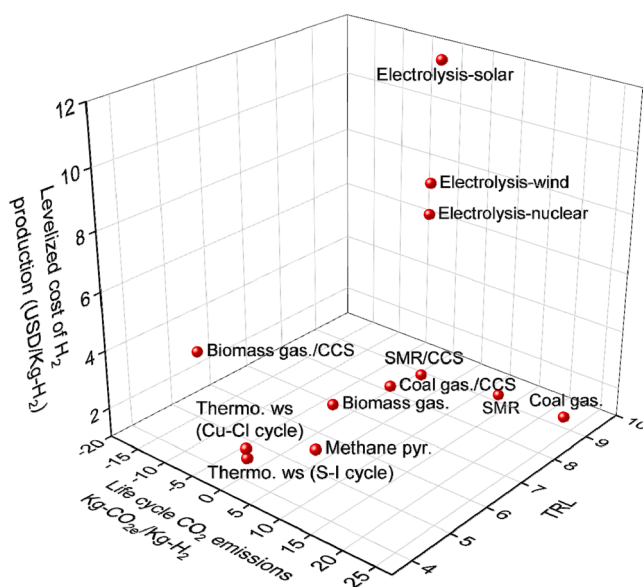


Fig. 1. Comparison of different H₂ production technologies for life cycle CO₂ emissions, levelised cost of H₂ production, and TRL [12]. Note: Gasification (gas.); Pyrolysis (pyr.); Thermochemical water splitting (Thermo. ws).

OCs, including their detrimental behaviour with the components of biomass ash and limited gas–solid interaction efficiencies with feedstock volatiles. However, since the beginning of this century, the research community has witnessed an exponential growth of publications in the CLP domain, truly indicative of a renewed interest [16].

According to the type of OCs and target output, CLP can be categorized as follows [1,17]:

1. In type A, oxygen is indirectly provided to the feedstock using metal oxides or sulphates as OCs. It can be further divided based on target output: (i) to generate heat/electricity, so-called chemical looping combustion, and (ii) to generate fuels such as syngas or H₂, so-called biomass chemical looping gasification (BCLG).
2. In type B, the OC is a sorbent similar to CaO. The sorbent adsorbs CO₂ from the produced gas stream in one reactor and desorbs in another reactor. Such a process is called calcium looping gasification.

2. Biomass chemical looping gasification

2.1. Process Overview

The BCLG process is similar to the circulating fluidized bed gasification (CFBG) process. In the case of CFBG, biomass is gasified using two connected reactors: (i) a gasification reactor in which biomass is gasified using steam, and (ii) a combustion reactor in which residual char from the gasifier is combusted to supply heat for the gasification reactions, which is transported using an inert circulating bed material [18–20]. In contrast, BCLG transports lattice oxygen using OC materials (e.g., metal oxides). The OC materials circulate between the two coupled fluidised bed reactors, carrying oxidised carrier and heat from the air reactor to the fuel reactor. In such a process, the OC is reduced in the fuel reactor and recycles back to the air reactor for regeneration (Fig. 2) [21–23].

Understanding the pathways of gasification reactions is fairly challenging due to the complexities inherent in biomass physio-chemical properties. A general outline of the reactions involving iron oxide as an OC has been conceptualised in Fig. 3 [5,13,24] and further summarised in Table 1 [24–26], providing a reasonable insight into the reaction chemistry. In the fuel reactor, firstly, biomass gets pyrolysed into three phases, starting with primary pyrolysis, wherein biomass gets thermally degraded into char, tar, and volatile gases (R1), after which

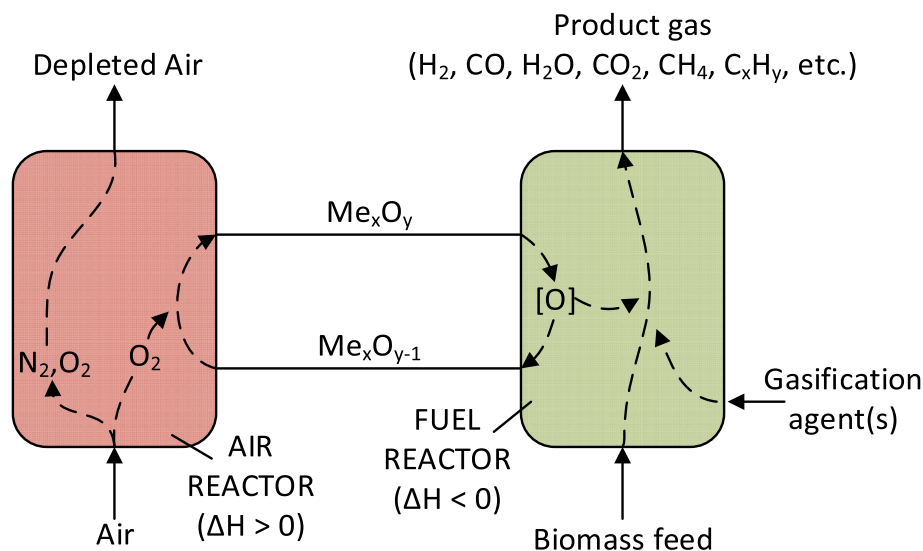


Fig. 2. Schematic diagram of BCLG.

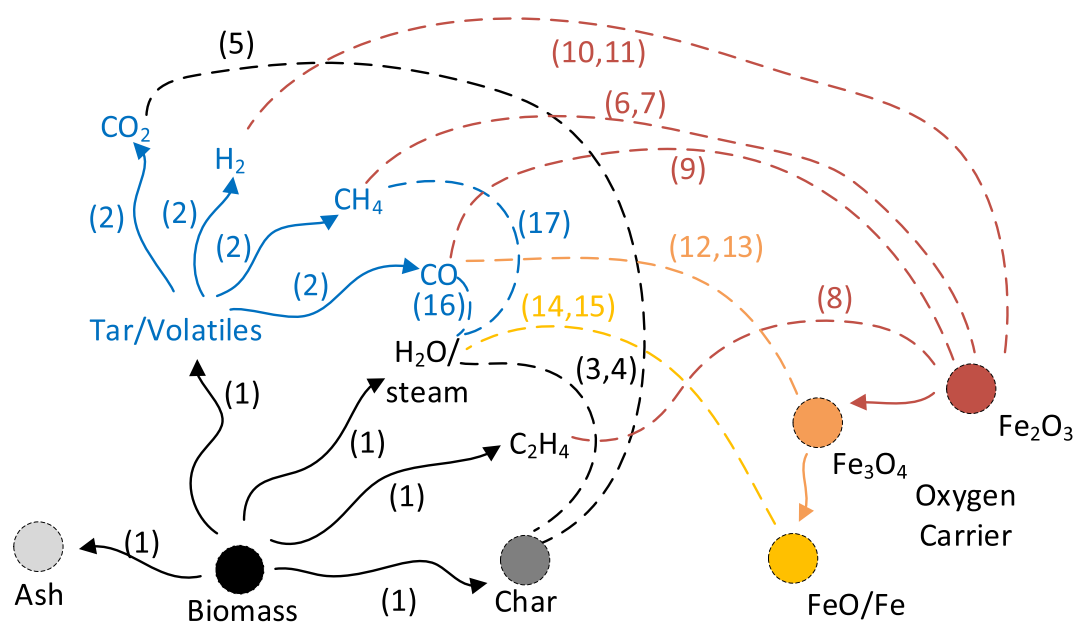


Fig. 3. Reaction pathways in the fuel reactor.

tar from biomass is further cracked to generate additional volatiles (R2); and then the gasification agents, including H_2O and CO_2 , which provide fluidisation of the bed particulates, participate in the char gasification reactions (R3, R4, R5) as reactants [21,24,27]. Simultaneously and in parallel reaction pathways, the OC is reduced and supplies the lattice oxygen for partial/complete oxidation of volatiles, decreasing the process endothermicity and enhancing gasification kinetics (R6–11) [21,22,28]. Furthermore, Fe_3O_4 in contact with the CO generated from char gasification reactions (R3) [29] can be reduced to FeO and Fe according to R12 and R13. Steam supplied as a gasification agent also partially oxidises FeO/Fe to Fe_3O_4 through the iron-steam reactions (R14, R15) [30,31]. Moreover, the homogenous steam-methane reforming and water-gas shift reactions occur in the gas phase, improving the quality of the syngas produced (R16, R17) [25]. Finally, the reduced OC is circulated back to the air reactor, where it is regenerated in the presence of oxygen (R18, R19) [21,27,32]. Along with the OC, some unconverted char may enter the air reactor, which reacts with oxygen to produce carbon dioxide (R20).

2.2. BCLG characteristics

In the following section, we elaborate the key features of BCLG and compare it to conventional biomass gasification.

- (1) Generally, conventional gasification systems use pure oxygen to produce syngas [33]. An expensive and high maintenance air separation unit (ASU) is needed to provide oxygen, affecting plant efficiency and process economics [33]. In addition, CO_2 and steam are used as gasification mediums [34–37]; still, the process encounters slow gasification kinetics and requires a large amount of heat, thus limiting its efficiency [27,33,38]. With BCLG, the process cost can be significantly reduced by eliminating the use of ASU while using a low-cost OC to provide lattice oxygen [5,26].
- (2) For conventional gasification, if the air is supplied as a gasification agent, nitrogen in the air can dilute the syngas, affecting its quality. Using an OC instead of air to gasify the biomass could

Table 1

Reactions in the fuel and air reactor.

Reaction equation	No.
Reactions in the fuel reactor	
Biomass → Char + Ash + Tar + Volatiles + H ₂ O	(R1)
Tar → CH ₄ + CO + CO ₂ + H ₂	(R2)
C + H ₂ O ↔ CO + H ₂ (ΔH = +131 MJ/kmol)	(R3)
C + 2H ₂ O ↔ CO ₂ + 2H ₂ (ΔH = +90.1 MJ/kmol)	(R4)
C + CO ₂ ↔ 2CO (ΔH = +172 MJ/kmol)	(R5)
12Fe ₂ O ₃ + CH ₄ → CO ₂ + 2H ₂ O + 8Fe ₃ O ₄ (ΔH = +141.63 MJ/kmol)	(R6)
Fe ₂ O ₃ + CH ₄ → CO + 2H ₂ + 2FeO (ΔH = +244.4 MJ/kmol)	(R7)
8Fe ₂ O ₃ + C ₂ H ₄ → CO + CO ₂ + H ₂ + H ₂ O + 4Fe ₃ O ₄ + 4FeO (ΔH = +233.7 MJ/kmol)	(R8)
3Fe ₂ O ₃ + CO → CO ₂ + 2Fe ₃ O ₄ (ΔH = -47 MJ/kmol)	(R9)
Fe ₂ O ₃ + H ₂ → H ₂ O + 2FeO (ΔH = +38.42 MJ/kmol)	(R10)
3Fe ₂ O ₃ + H ₂ → H ₂ O + 2Fe ₃ O ₄ (ΔH = -6 MJ/kmol)	(R11)
Fe ₃ O ₄ + CO → CO ₂ + 3FeO (ΔH = +19 MJ/kmol)	(R12)
Fe ₃ O ₄ + 4CO → 4CO ₂ + 3Fe (ΔH = +13.6 MJ/kmol)	(R13)
3FeO + H ₂ O → H ₂ + Fe ₃ O ₄ (ΔH = -60.56 MJ/kmol)	(R14)
3Fe + 4H ₂ O → 4H ₂ + Fe ₃ O ₄ (ΔH = -37.77 MJ/kmol)	(R15)
CO + H ₂ O ↔ CO ₂ + H ₂ (ΔH = -41 MJ/kmol)	(R16)
CH ₄ + H ₂ O ↔ CO + 3H ₂ (ΔH = +206 MJ/kmol)	(R17)
Reactions in the air reactor	
4Fe ₃ O ₄ + O ₂ → 6Fe ₂ O ₃ (ΔH = -471.96 MJ/kmol)	(R18)
4FeO + O ₂ → 2Fe ₂ O ₃ (ΔH = -560.5 MJ/kmol)	(R19)
C + O ₂ → CO ₂ (ΔH = -393.5 MJ/kmol)	(R20)

improve the produced syngas quality and mitigate NO_x emissions [17,39].

- (3) In the case of BCLG, reduction products of OCs formed in the fuel reactor can act as catalysts and promote tar cracking. It improves syngas quality with relatively low tar content [40–43]. At the same time, some OCs act as a catalyst to convert precursors of NH₃ and NO_x into N₂, which reduces nitrogen oxide emissions [44,45].
- (4) BCLG appears to be more efficient and relatively cheaper than conventional gasification technologies. A techno-economic analysis of 7-MWth systems concluded that the BCLG unit annual operating cost was USD 0.58 million less than conventional biomass combustion and gasification unit [46]. Furthermore, the BCLG process for hydrogen and electricity co-production is 10–25 % more efficient than conventional systems [47]. Moreover, biomass-based integrated gasification combined cycle (BIGCC) coupled with chemical looping was 2–4 % more efficient than an existing BIGCC plant in China [38].

BCLG is an economical, efficient and low-emission technology that can overcome the shortcomings of conventional biomass gasification and presents an excellent potential to utilise biomass resources sustainably. There are several review articles discussing the experimental, design and material research of CLP [48–56]. However, review articles focusing in particular on BCLG have rarely been published in open literature [26,57] and still lack critical detailed discussions. Therefore, this work systematically examines the available experimental and modelling research studies on BCLG technology. Firstly, the effect of process parameters (e.g., fuel reactor temperature, gasification agent, OC, reactor configuration) was profoundly investigated on the gasification performance (e.g., carbon conversion and gasification efficiency, product gas composition, and lower heating value). Secondly, the performance of different OCs in the BCLG process was extensively examined and compared them for essential characteristics such as reactivity, agglomeration, sintering, oxygen transport capacity, cost, and environmental friendliness. Thirdly, the mathematical modelling studies were discussed to understand the thermodynamic, kinetic and overall process behaviour of BCLG. Next, the BCLG was critically approached by discussing the technological challenges and future research needs related to the OC, reactor system, biomass ash and mathematical modelling. Lastly, the potential of BCLG technology was highlighted to offer unique prospects of a decarbonised circular economy.

3. Experimental approach

3.1. Experimental Overview

Mendiara et al. [5] stated that the first BCLG operation was performed by Matsuoka et al. [58] in 2006 using oakwood sawdust in a fluidised bed reactor with iron oxide-impregnated porous γ-alumina at 500–700 °C. The results indicated that adding iron oxide to the alumina increased H₂ production at all the measured temperatures. Since then, BCLG has been the subject of numerous experimental and analytical studies [28,59–64].

In the past, multiple studies were conducted on the BCLG of varied biomass (such as pine, rice straw/husk, wheat straw, polyethylene, sewage sludge) using multiple OCs (e.g., copper ore and slag, hematite, red mud, CaO, Fe₂O₃, Al₂O₃ and NiO). In addition, different reactor systems, including fixed bed, TGA, bubbling, and circulating fluidised bed in both batch and continuous modes were explored. Table 2 summarises the BCLG experimental studies, which are discussed in detail in a supplementary document. In addition, the authors studied the influence of reactor temperature, time, OC, steam, and number of redox cycles on the gasification performance. Moreover, the OCs were examined using a series of characterisation methods such as XRD, X-ray fluorescence (XRF), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) spectroscopy, temperature programmed oxidation and reduction (TPO and TPR), and Mössbauer spectroscopy techniques. Section 3.2 and 3.3 discuss such parameters in detail. It was observed that several mineral elements such as Na, K, Ca, and Fe in OCs catalysed the gasification performance due to enhanced char and tar cracking. Furthermore, the reactivity was found to occur in the following order O₂ ≈ NiO > H₂O > Fe₂O₃ > CO₂ > Al₂O₃ [65]. Interestingly, the studies recommended using industrial waste as OCs to reduce air pollutant emissions during gasification, as decreased concentrations of HCN, NH₃, NO, and SO₂ in the product gas were observed due to the presence of alkaline CaO and Na₂O [66].

Operating conditions play a vital role as they influence the process performance. Sub-section 3.2 discusses the effect of the most important process parameters (such as fuel reactor temperature, gasification agent and OC) on the BCLG process. Data to analyse the impact of the process parameters drawn from the experimental studies is discussed in sub-section 3.1.

3.2. The impact of process parameters on BCLG

3.2.1. Fuel reactor temperature

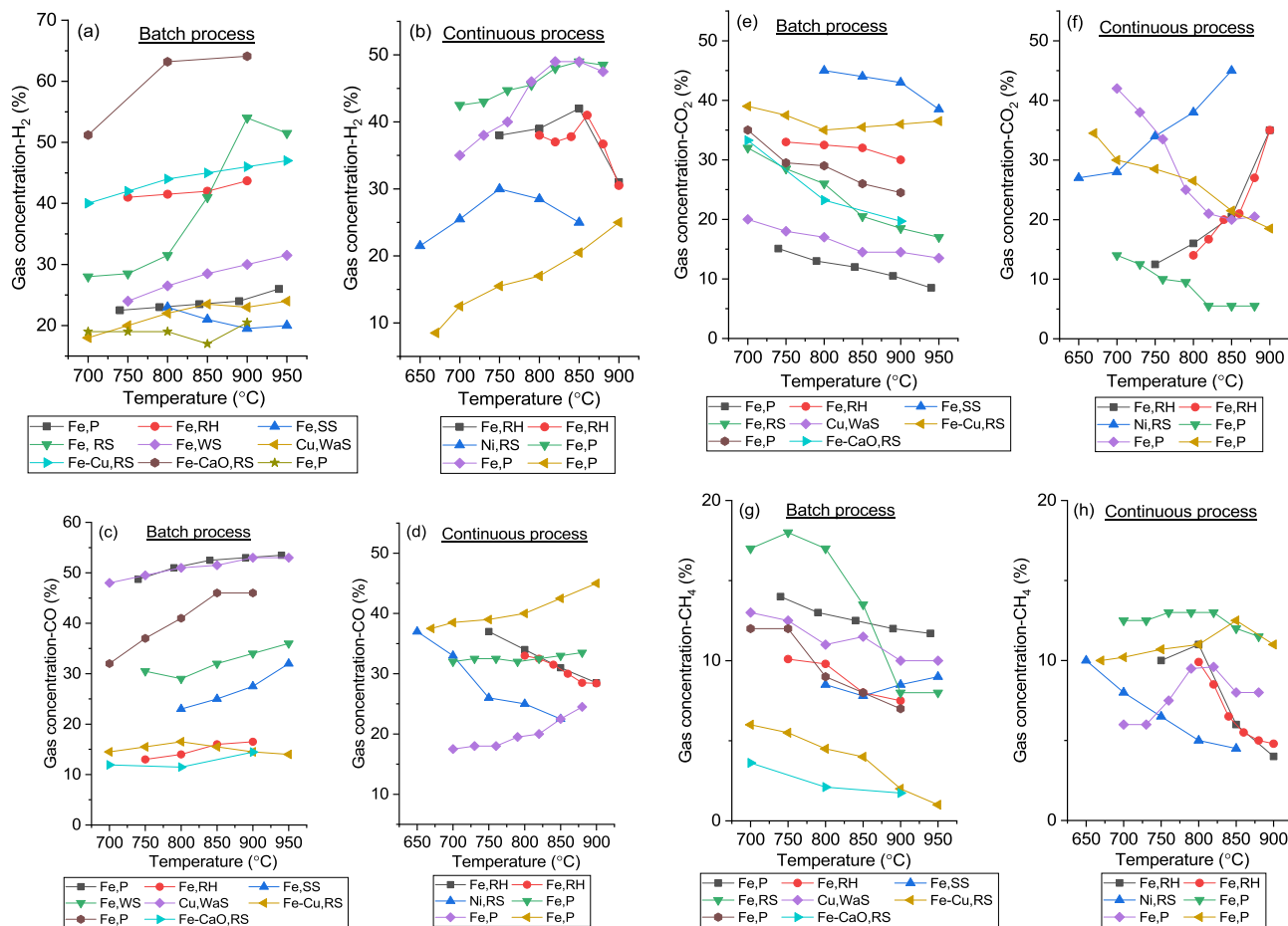
The fuel reactor temperature is an essential variable for the BCLG of biomass. In the present work, the relationship between fuel reactor temperature and the concentration of product gases such as H₂, CO, CO₂, and CH₄ were examined and compared using the data from selected experimental studies in the literature [29,32,39,67,73,81,82].

Fig. 4a and 4b present the variation of H₂ concentration as a function of fuel reactor temperature. In the case of a batch reactor, H₂ concentration monotonously increased with the temperature in most cases. The possible explanation is that higher temperature favoured the reactants for exothermic reactions and products in endothermic reactions (Le Chatelier's principle) [74]. Although a higher temperature would push the water–gas shift reaction (R16) towards the reactants, thereby consuming H₂, nonetheless the reactions (R3, R17) are endothermic, and higher temperatures would favour the formation of H₂. Moreover, an increased amount of H₂ is generated as the rate of tar cracking (R2) accelerates with increased temperature. Nevertheless, the variation of H₂ is not uniform, as the study conducted by Huang et al. [74] displayed an opposite trend. The authors used sewage sludge and natural hematite in a fixed bed batch reactor for BCLG experiments. It was argued that the redox reaction (R10) is endothermic, and an increase in temperature would push the equilibrium towards the product, thereby decreasing the

Table 2

Overview of selected BCLG experimental studies conducted in the past.

Process	Reactor type	Feedstock	OC(s)	Reaction conditions	References
Continuous	Interconnected dual FB reactors	Pinewood, Pine sawdust, Rice husk, Rice straw	Iron-olivine, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\cdot\text{NiO}/\text{Al}_2\text{O}_3$, $\text{NiO}/\text{Al}_2\text{O}_3$, $\text{CaO}\cdot\text{NiO}/\text{Al}_2\text{O}_3$	Temperature: 650–1000 °C OC/feed: $\approx 4\text{--}20$ LM/BM: $\approx 0.2\text{--}0.6$	[39 42 67 64 68]
Batch	Coupled BFB and CFB reactor, Fixed bed, Fluidized bed, TGA	Biomass sawdust, Polyethylene, Pine char, Pine sawdust, Sewage Sludge, Wheat straw, Rice straw, Rice husk	CaO , NiO , Fe_2O_3 , $\text{Fe}_2\text{O}_3\cdot\text{support}$ (Al_2O_3 , SiO_2 , TiO_2 , ZrO_2), Hematite, $\text{NiO}\cdot\text{Fe}_2\text{O}_3$, Red mud, $\text{Fe}_2\text{O}_3/\text{CuO}$, $\text{Fe}_2\text{O}_3/\text{CaO}$, Sludge ash, Copper slag, Copper ore	Temperature: 30–1200 °C OC/feed: $\approx 0.2\text{--}11.5$	[2728 29 65 6761 66 69 70 71 72 73 74 75 76 77 78 79 80]

**Fig. 4.** Effect of temperature on (a/b) H_2 , (c/d) CO , (e/f) CO_2 and (g/h) CH_4 concentration (%) for different OCs and feedstock using batch/continuous processes, respectively [29,32,39,67,68,73,74,77–79,81–83].

H_2 concentration. In the case of continuous reactors, H_2 concentration increased with temperature to reach a maximum and then decreased at higher temperatures (750–850 °C). At first, the H_2 concentration increased slowly due to the accelerated tar cracking (R2) rate, compensating for H_2 loss as consumed in the redox reaction (R10). In addition, the water–gas reaction (R16), which became aggravated, pushed to the reactant side with increased temperature at the expense of H_2 . This resulted in a decline in H_2 concentration at higher temperatures.

As shown in Fig. 4c and 4d, in the case of batch reactors, the concentration of CO increased with increasing fuel reactor temperature. This is because an increase in temperature shifts the equilibrium for reactions (R3, R5, R17) towards the product side while moving the equilibrium of the water–gas shift reaction (R11) towards the reactant

side. Furthermore, in the case of continuous reactors, the concentration of CO decreased with temperature in most cases. This is attributed to the faster rate of CO consumption for reduction of OCs (R12, R13) at elevated temperatures. However, results from some studies [39,81,83] using a continuous reactor displayed an opposite trend as the studies did not account for rapid CO consumption due to the reduction of OCs. Here it is noteworthy that in the experiments performed by Shen et al. [77], the relative concentration of CO increased until 800 °C and then decreased between 800 and 950 °C. The change of trend can be attributed to dominant reactions (R21, R22). In addition, due to the oxygen uncoupling characteristic of CuO , more char was completely rather than partially oxidised, thereby decreasing the CO concentration and increasing CO_2 concentration (Error! Reference source not found.).

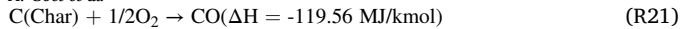


Fig. 4e and 4f present the effect of temperature on CO₂ concentration for both batch and continuous reactor systems. For batch reactors, CO₂ concentration decreased with the increased temperature as the equilibrium of water gas-shift reaction (R16) moved towards the reactant, resulting in a gradual decrease of CO₂ concentration. On the other hand, CO₂ concentration increased with increased temperature for continuous reactors due to the faster rate of OC reduction reactions (R12, R13) and the gasification reaction (R4). However, for some research studies [39,81,83] using continuous reactor systems, the CO₂ concentration decreased with increasing temperature. This is because of the higher CO₂ consumption rate due to the Boudouard reaction (R5) and the lower CO₂ production rate due to the restricted lattice oxygen supply by the OC.

The change in concentration of CH₄ as a function of temperature is presented in Fig. 4g and 4h. For both kinds of reactor systems, CH₄ concentration initially showed an upward trend but later decreased with an increase in temperature. This is because CH₄, mainly produced from biomass pyrolysis at an early stage, gets offset by the intensive endothermic reactions (R6, R7, R17) at elevated temperatures.

CCE, Cold Gas Efficiency (CGE), LHV of product gas, and total gas yield are critical to investigating reactor behaviour. Fig. 5 presents the variation of the parameters (mentioned above) as a function of fuel reactor temperature. The values for all four parameters increased with increasing temperature. The results indicate that increased temperature improved biomass gasification, increasing CCE, CGE, LHV, and gas yield. Additionally, high temperatures can provide favourable conditions, thereby accelerating endothermic reactions such as steam reforming and thermal cracking of tar, which converts more carbon and hydrogen into product gas [84–86]. Interestingly, the CCE showed a slight decrease at higher fuel reactor temperatures (850–950 °C) for some research studies [75,77]. Sintering and agglomeration of OC could be a reason for the decrease as it would reduce the contact between solid OC and produced gases and prevent the OC from releasing oxygen, thereby decreasing the reactivity of OC [77,87].

3.2.2. Gasification Agent: Steam

Steam can act as a good gasification agent and provide molecular oxygen to promote char conversion. More importantly, adding steam helps improve the quality of syngas by generating a high concentration of H₂. Consequently, some authors investigated the utilisation of steam as a gasification agent in BCLG, and the results are presented below. Hereafter, steam to biomass ratio (SBR) refers to the quantity of steam introduced in the reactor to the mass of fed biomass.

Furthermore, to evaluate the effect of SBR on the product gas, Fig. 6a, 6b, 6c and 6d present the variation of H₂, CO, CO₂, and CH₄ concentrations with the SBR ratio. With the addition of steam, in most cases, H₂ and CO₂ concentrations increased, while CO and CH₄ concentrations displayed a downward trend. Additionally, the CH₄ gas concentration was the lowest for all the studies considered. Due to the increase in SBR, the water gas-shift reaction (R16) moves towards the product side, increasing the H₂ and CO₂ concentration and decreasing the CO concentration. In addition, the addition of steam elevated the H₂ production due to the water–gas reaction (R3) promoted towards the product side. Finally, the steam methane reforming reaction (R17) shifted towards the product due to an increase in SBR and decreased the CH₄ concentration. More importantly, the trend in the variation of product gas concentrations was similar for both batch and continuous reactor systems.

The variation trend of CCE versus SBR is shown in Fig. 6e. The results illustrate that CCE increased initially with SBR; after the SBR ratio value became too high, the CCE started declining. Initially, with the increase in SBR, the endothermic reactions (R3, R4, R17) moved towards the product side, thereby accelerating the conversion of carbon to the gaseous product. Moreover, the addition of steam promoted the water–gas shift reaction and tar cracking. However, after SBR exceeded a particular value, the fluidisation velocity in the steam reactor increased significantly, leading to the elutriation of char particles [87]. More importantly, the addition of excessive steam would require a large amount of heat to elevate the steam temperature. Consequently, the overall temperature of the reactor would drop, impeding the process of biomass gasification, thereby decreasing the CCE [88,89].

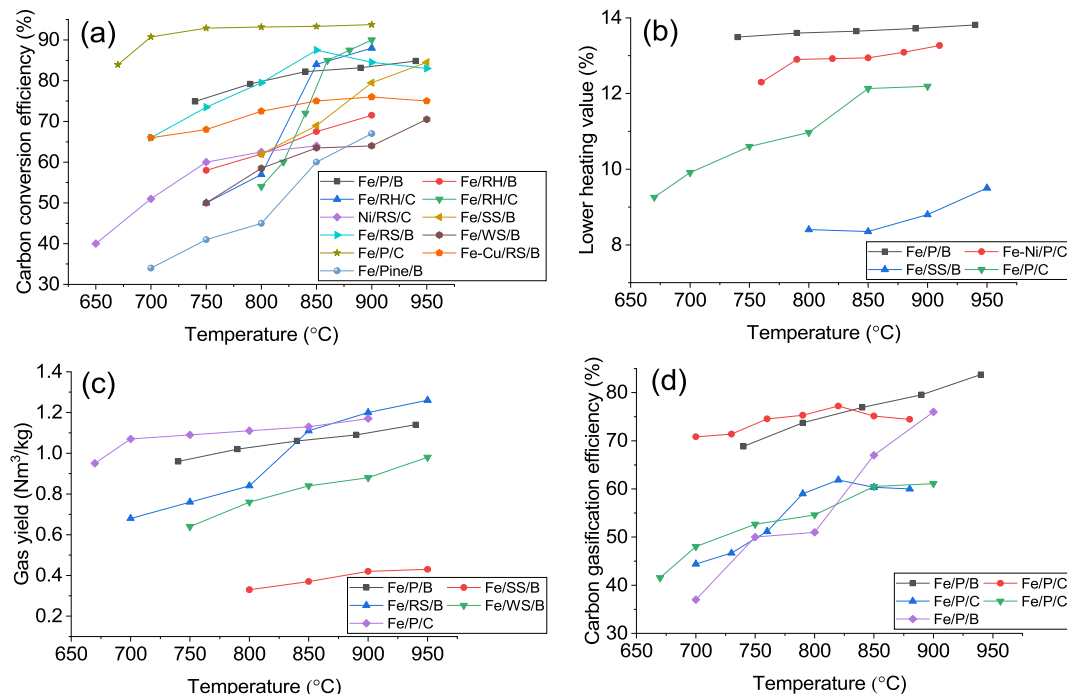


Fig. 5. Effect of temperature on CCE/LHV/CGE/gas yield for different OCs and feedstocks [29,32,39,67,68,73,74,77–79,81–83].

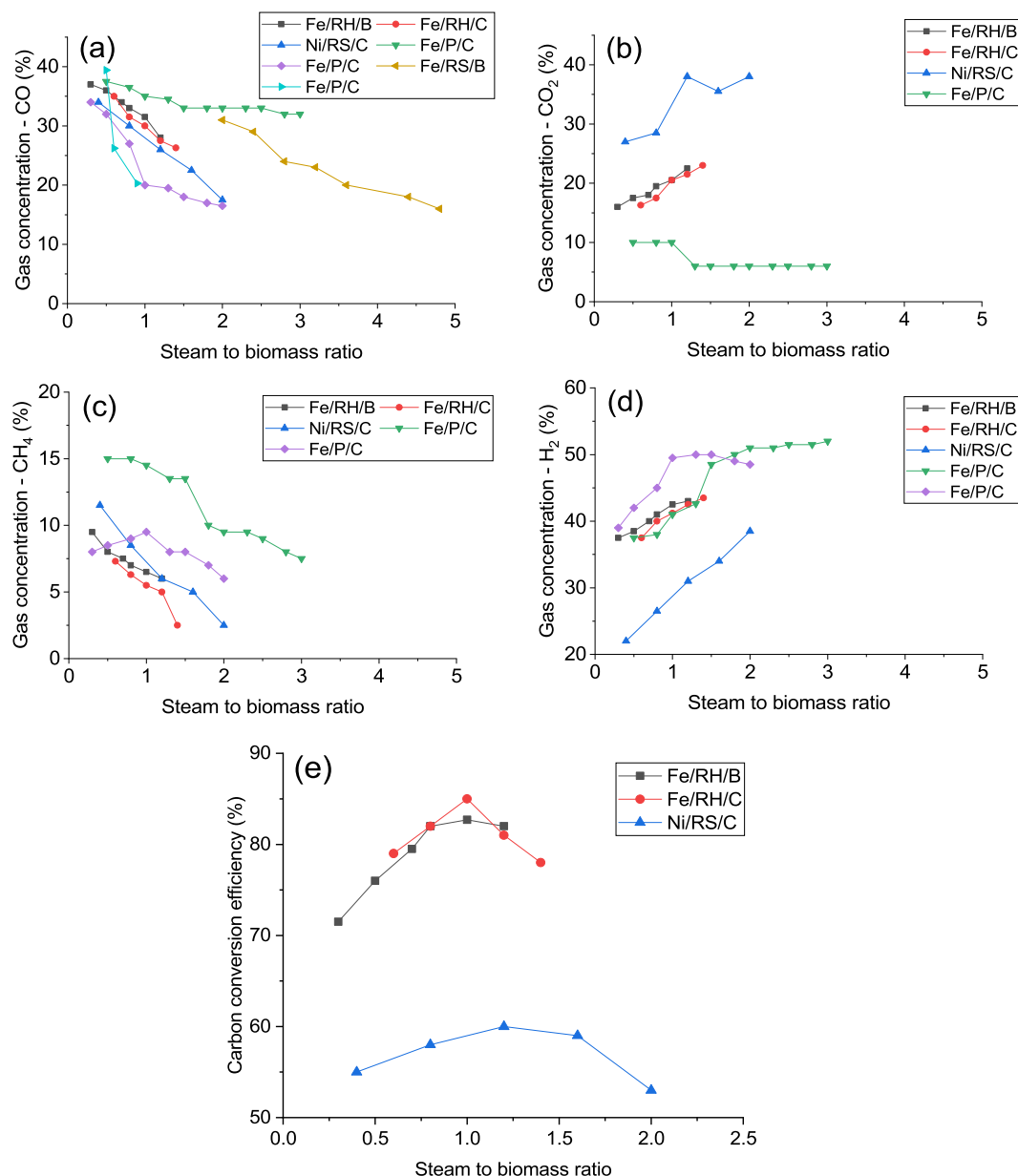


Fig. 6. Effect of SBR on (a) CO, (b) CO₂, (c) CH₄, (d) H₂ concentration and (e) carbon conversion efficient for different OCs and feedstock [32,42,67,68,75,83].

3.2.3. OC quantity

In addition to being heat carriers and catalysts, OCs act as an oxygen source for biomass gasification, which affects the performance of the BCLG process, including gas yield, quality, and product gas composition. In the past, several definitions (e.g., mass ratio of OC to biomass, molar ratio of OC to biomass, molar ratio of oxygen content in OC to biomass carbon content) were used to evaluate the effect of OCs. In general, it was observed that increasing the amount of OC in the BCLG process promotes char and tar cracking and char gasification, thereby improving the carbon conversion efficiency. However, excessive quantities of OC lead to over oxidation of syngas (H₂ and CO), thereby lowering the LHV. Altogether, the quantity of OC used in the BCLG process needs careful optimisation to balance the CCE and LHV, thereby maximising the gasification efficiency.

Wei et al. [39,64] and Huang et al. [73] studied the effect of OC content on the BCLG process in a continuous fluidised bed reactor by varying the biomass feeding rate while keeping the OC feed constant. They observed that increasing the biomass feeding rate increased H₂, CO, and CH₄ concentrations and decreased CO₂ concentration.

Furthermore, with the increase in biomass feeding rate, the dominant pyrolysis reaction increased the CH₄, CO, and H₂ concentrations, which could not completely react with the limited lattice oxygen to form CO₂ and H₂O. The decreasing trend of CCE values and the increasing trend of LHV values can be similarly explained.

Two studies conducted by Ge et al. [32,67] investigated how the hematite mass-percentage increase in the bed affected the BCLG process. They concluded that a considerable mass percentage (e.g., greater than 40 % mass in their study) is required to maintain stable gasification temperature. Moreover, they reported that increasing the mass percentage of hematite decreased the H₂, CO, CH₄, and C₂H₄ concentrations while increasing the CO₂ concentration. Furthermore, CCE increased, and syngas (CO + H₂) yield decreased with the increase in hematite percentage. An increase in supply of OC promotes the water-gas shift (R16) and tar cracking (R2) reactions to generate H₂ and CO. However, significant amounts of H₂ and CO are also consumed by reactions R10-R11 and R9-R12, respectively, thereby decreasing their concentrations and consequently the syngas yield. The decrease in CH₄ concentration can be attributed to the reduction reaction (R9). In addition, CCE

increased with an increase in OC due to the consumption of gasification products ($\text{CO} + \text{H}_2$) which would stimulate the char gasification reaction (R3).

In this section, the impact of varied process parameters was assessed on BCLG and optimised for high-quality syngas. It was concluded that fuel reactor temperature should lie between 700 and 800 °C. This is because the increase in fuel reactor temperature positively increased the LHV, CCE, CGE and product gas yield. However H_2 concentration decreased at temperatures higher than 750–800 °C. Furthermore, the SBR should lie between 0.5 and 1.1 as CCE decreased and H_2 concentration did not significantly increase with higher SBR values. Moreover, a higher mass percentage of OCs (at least 40 %) is required in the reactor to maintain a stable gasification temperature.

3.3. Properties and screening of OCs

OC are chemical intermediates that indirectly provide lattice or molecular oxygen to the biomass feedstock without letting air come into direct contact with the feed. OCs can be classified based on their type, and Table 3 illustrates the type of OC and the examples reported in BCLG experiments discussed in section 3.1.

3.3.1. Characteristics of OCs

- (1) Compared to conventional gasification where the heat is supplied by the combustion of carbon, OC can act as a thermal source for BCLG. During the BCLG process, the OC particles in the interconnected fluidised beds are heated up in the air reactor, releasing heat in the fuel reactor. However, heat management in the BCLG process is more complicated than chemical looping combustion (CLC) due to the partial oxidation of fuel to produce syngas (i.e., CO and H_2) rather than complete oxidation in CLC. Therefore, to effectively manage the heat between the two reactors, it becomes imperative to control the circulation of OC particles. The circulation of OC particles depends on the fluidisation velocities of the two FB reactors, their exit geometry, and the properties of OC [106].
- (2) Calcium oxide, when present as OC in BCLG, can adsorb CO_2 and crack tar to produce H_2 -rich syngas [99,103,107–109]. Furthermore, it was reported that using a $\text{CaO}/\text{Fe}_2\text{O}_3$ mixture as OC produced approximately three mmol/g-biomass higher H_2 than pure Fe_2O_3 [110]. Furthermore, it was observed an improvement of 78.98 % H_2 yield by using a $\text{CaO}/\text{Fe}_2\text{O}_3$ mixture as an OC [111]. However, some studies reported deactivation of CaO post-adsorption of CO_2 , which poses a significant issue for continuous

H_2 production, and frequently replacing CaO may not be economically viable for the process [112].

- (3) The OC can catalyse the gasification reactions due to inorganic compounds [1]. Moreover, the BCLG benefits from the reduced tar generation, which is a major concern with conventional gasifiers. Fig. 7 compares the effect on tar generation due to the use of OC. Pine wood/sawdust was used as gasification feed, and the results are shown for reactor temperatures between 800 and 920 °C. The figure clearly shows that the tar generation using OC was much lower (nearly 2.5 times) than using inert bed material [80,113–115].

3.3.2. Screening of OCs

The performance of OC materials is imperative in determining the effectiveness of the BCLG process. Therefore, selection of an appropriate OC suitable for the efficient performance of BCLG is essential and should meet several criteria such as redox kinetics, oxygen transport capacity, resistance to contaminants and carbon deposition, mechanical strength and melting point [116]. The following section compares and discusses these criteria for varied OCs.

3.3.2.1. Redox potential. Previously, Ellingham and modified Ellingham diagrams (Fig. 8) were used to study the redox behaviour of metal oxides used in various chemical looping processes [50,117]. Ellingham diagrams theoretically depict the redox potential of different metal oxides based on the standard Gibbs free energy of the reactions. They provide theoretical indications for selecting appropriate OCs based on the end-product requirements such as partial or full oxidation of the feedstock. The Ellingham diagram is modified into three zones (Fig. 8b) based on the three critical reactions (R22, R23, R24). Zone A represents the combustion zone (above reaction line (R22)), and the metal oxides (e.g., NiO , Cu_2O , CuO , CoO , Fe_2O_3 and Fe_3O_4) falling in this zone presents strong oxidising potential and may be used to fully/partially oxidise the feedstock. Alternatively, zone B represents the syngas production zone (between reaction lines (R22) and (R23)), and the metal oxides (e.g., Ce_2O_3) lying in this zone can theoretically only produce CO and H_2 , thereby making it ideal for partial oxidation of the feedstock. Finally, zone C represents the inert zone, and the metal oxides (e.g., Cr_2O_3) present in this zone have limited oxidising capability and therefore are considered inert for CLPs. Ellingham and modified Ellingham diagrams use reaction thermodynamics for preliminary screening of OCs, however, they have limited applications in assessing the reaction thermodynamics of OCs with multicomponents.

Table 3
Classification of OCs used in different BCLG experiments.

Catagories	OCs used in different BCLG experiments	
Transitional metal oxides	Monometallic oxides	Fe_2O_3 [90], CuO [91], NiO [68]
	Polymetallic oxides	LaFeO_3 [92], NiFe_2O_4 [93], MnFe_2O_4 [92], BaFe_2O_4 [94], CaFe_2O_4 [95], CoFe_2O_4 [96], $\text{Ca}_2\text{Fe}_2\text{O}_5$ [78]
	Oxide mixtures	$\text{Fe}_2\text{O}_3 - \text{K}_2\text{CO}_3$ [97], $\text{Fe}_2\text{O}_3 - \text{NiO}$ [64], $\text{Fe}_2\text{O}_3 - \text{CuO}$ [77], $\text{Fe}_2\text{O}_3 - \text{CaO}$ [98,99], Copper ore [80], Hematite [27,32,71,73], Manganese ore [100]
Ores	Natural ores	$\text{Fe}_2\text{O}_3 - \text{NiO}$ [28], CuFe_2O_4 [80]
Industrial waste	Modified ores	Copper slag [76], Red mud [66,101], Fe_2O_3 rich-sludge ash [79], Steel converter slag [102]
		Al_2O_3 [39], MgO [103], SiO_2 [104], TiO_2 [29], ZnO [103], ZrO_2 [105], Calcium aluminate cement [77]
Inert support		

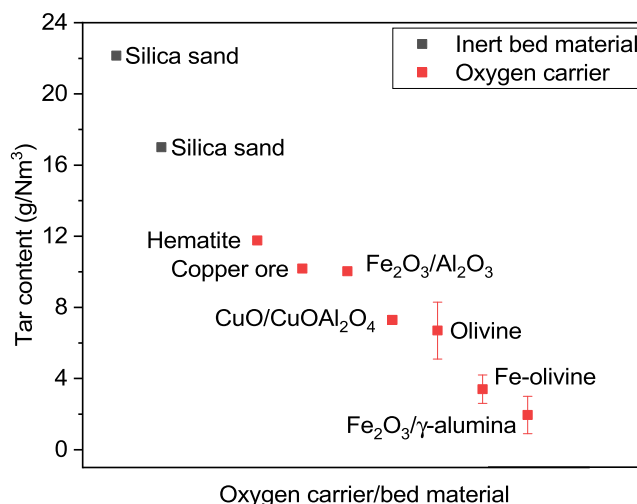


Fig. 7. Tar content comparison of bed material and OCs [80,113–115].

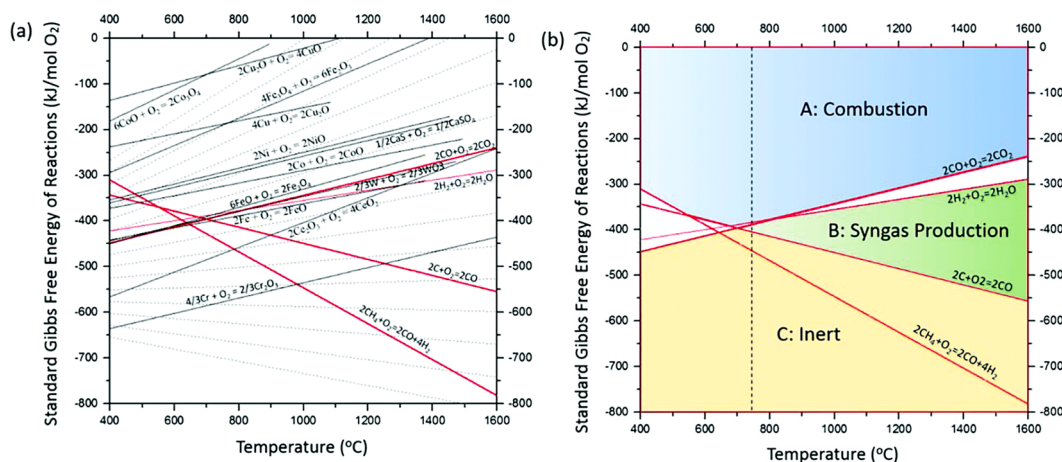
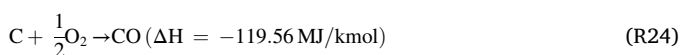
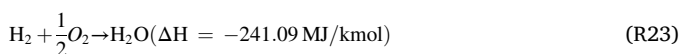


Fig. 8. (a) Ellingham and (b) modified Ellingham diagram to select the appropriate OC based on end-product requirement. Both (a) and (b) are reprinted from Zhao et al. [1].



3.3.2.2. Oxygen transport capacity (OTC). OTC is a vital parameter in understanding the suitability of OC for the BCLG process and is defined as the amount of available lattice oxygen from the OC under chemical looping conditions. In addition, OTC values are useful in studying reactor sizing, efficiency and economics as OTC values are inversely proportional to the solid circulation rate and bed inventory between the two reactors. Fig. 9 shows the OTC values of the commonly used OCs in BCLG. Among the considered OCs, CaSO₄/CaS, Fe₂O₃/Fe, NiO/Ni, Co₃O₄/CoO/Co, and CuO/Cu have relatively high OTC values. However, a higher OTC value does not always guarantee a high gasification efficiency as the amount of oxygen transported from air to fuel needs careful moderation to prevent the oxidation of syngas which reduces its heating value. In such cases, mixing OCs with inert support material can complement their higher OTC values, improving the carrier's performance [118].

3.3.2.3. Reactivity, Cost, Eco-friendliness and mechanical properties. In Fig. 10, important properties such as resistance to attrition and agglomeration, environment friendliness and non-toxicity, reactivity, and melting temperatures of multiple OCs are compared.

Fe-based metal oxides are among the most commonly studied OCs despite their lower reactivity and oxygen transport capacity (OTC) [1,57]. Moreover, Fe-OC forms an attractive option for BCLG operations because of its high sintering, resistance, low cost, environment friendliness, non-toxicity, low carbon deposition, and low sulphate/sulphide formation tendency [1,96,120–122]. However, due to its slow redox kinetics, low OTC, and fuel conversion, Fe-OC requires a higher circulation rate and support of inert materials (e.g., Al₂O₃, MgAl₂O₄, SiO₂, TiO₂, and ZrO₂) to improve the reactivity [21,123–126]. Nevertheless, Fe-based OC tended to agglomerate and form magnetite with an inverse spinel structure during reoxidation [93].

Although Ni-based metal oxides are not environmentally friendly, toxic, and relatively expensive, they offer the highest reactivity for redox BCLG reactions and high OTC [51,127,128]. However, pure NiO suffers from kinetic limitations on the reaction rate due to its low porosity [129]. Interestingly, it was found that the use of NiO can reduce NO_x emissions which is essential for biomass thermochemical conversion, and metallic Ni can promote char and tar cracking [130–132].

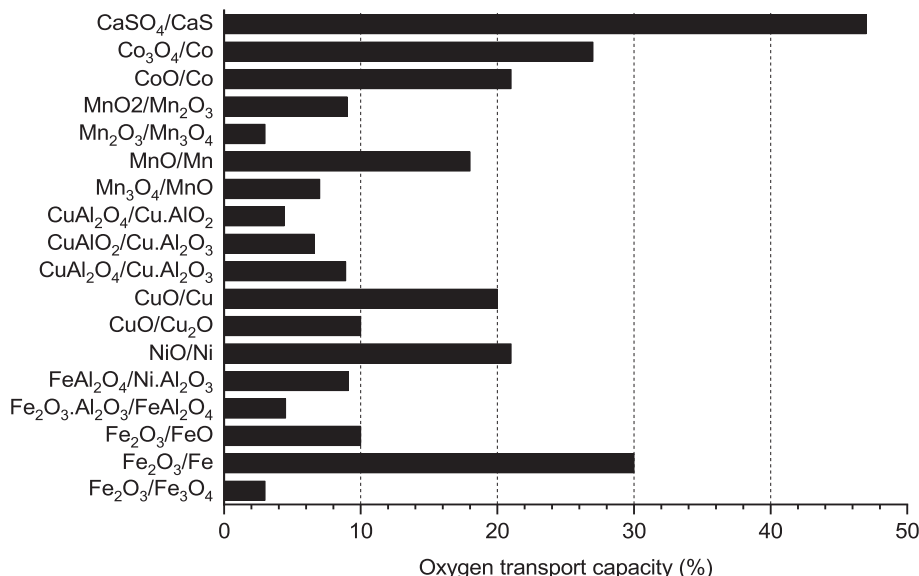


Fig. 9. OTC values of the commonly used OCs in BCLG [1,57,119].

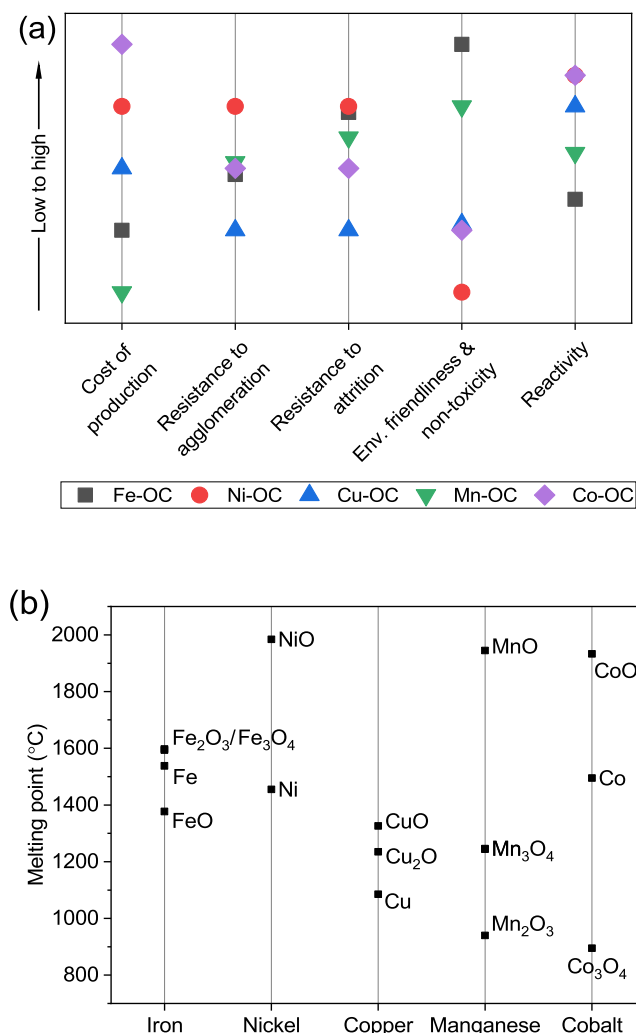


Fig. 10. Comparison charts of (a) cost of production, resistance of agglomeration and attrition, environment friendliness and non-toxicity, reactivity (b) melting temperatures for different OCs [1,26,55,57,91,115,119,121,122,129–133,139,141–143].

Nevertheless, Ni-OC offers low sintering and sulphur resistance due to the formation of NiS [119]. In addition, when NiO reacts with sulphur, Ni₃S₂ is formed, leading to sulphur poisoning [133].

Cu-based metal oxides provide good properties as OCs in the BCLG process, such as high reactivity and OTC and cyclicity. In addition, Cu-OC has higher OTC and reactivity than Fe-based OCs while being less toxic and cheaper than NiO [1,127]. However, the main disadvantage of Cu-OC is agglomeration and attrition due to metallic copper's low melting point and poor mechanical properties [127]. Therefore, it is essential to support CuO on inert materials such as SiO₂, TiO₂, and Al₂O₃ which provide good resistance against agglomeration, sintering, and attrition [1,119].

Similar to Fe-based OCs, Mn-based metal oxides are less toxic and cheaper but higher OTC [1,57]. Nonetheless, Mn-based OCs exhibited lower fuel conversion and oxidation rates, and demonstrated inferior mechanical stability and thermodynamic limitations [134,135]. Typical inert materials (e.g., SiO₂, Al₂O₃, or TiO₂) were applied as support material to improve the stability of Mn-based OC, yet the reactivity of formed OC was inhibited [136,137].

Co-based metal oxides are not extensively used/studied due to their toxicity, low mechanical strength (e.g., lower resistance to attrition), thermodynamic instability, and high cost [96,138]. Although CoO can serve as an OC due to its high reactivity and OTC, it can react with

common inert supports (e.g., Al₂O₃, MgO, and TiO₂) to form unreactive compounds (e.g., CoAl₂O₄, MgO.4CoO.6O, and CoTiO₃, respectively), thereby resulting in complete loss of reactivity [139,140].

In the presence of OC, the tar generation could be 2.5-fold less as compared to the CLG with only inert bed materials (Fig. 7). Thus, in order to screen and design appropriate OCs for specific BCLG, various typical OCs have been comprehensively evaluated in terms of cost of production, resistance to agglomeration, resistance to attrition, environmental friendliness, reactivity, and melting points (Fig. 10). As demonstrated in Fig. 10, despite the relatively lower reactivity, Fe-OC is widely regarded as a suitable OC in BCLG because of its distinct advantages in cost of production, environmental friendliness and resistance to attrition. Hence, technological, economic, and environmental assessments should be taken into holistic consideration to achieve commercial application of designed OCs, which will be discussed in detail thereafter.

3.4. Reactor design

The interaction between biomass and OC particles is crucial in the BCLG process. Therefore, the selection of an appropriate reactor design is essential for efficient operation. In particular, the two most important factors to better design the BCLG reactor system include (i) adequate interaction between air/OC in air reactor and OC/biomass in fuel reactor, and (ii) sufficient solid OC particle circulation between air and fuel reactors. To date, the majority of BCLG experimental studies have been performed in small-scale fixed bed and fluidised bed reactors. We have discussed such studies in the supplementary document.

In fixed bed reactors, the solid OC particles are stationary. The particles are alternatively exposed to the oxidising and reducing environment by switching the feed streams. This enables more efficient utilisation of OC as separation of gas and solid OC particles is not required. However, using fixed bed reactors for BCLG applications is not feasible due to (i) inadequate heat and mass transfer, (ii) limited mixing of gas/solid particles, and (iii) the complex feed stream switching system.

In the past, BCLG has been studied in fluidised bed systems, mostly in a batch-type configuration. However, BCLG studies were conducted using dual-fluidised bed continuous systems. Fluidised bed systems offer the advantage of better gas/solid interaction, uniform temperature distribution and higher heat/mass transfer over fixed-bed systems. However, the system faces challenges related to the transfer of unburnt char to the air reactor and particle segregation that can lead to poor fluidisation.

4. Modelling approach

Modelling is an important tool for technology development, which could help to predict products and optimise performance by overcoming potential challenges posed by real conditions. In spite of limited research, representative BCLG modelling studies will be reviewed in terms of thermodynamic equilibrium modelling, process modelling, and kinetic modelling.

4.1. Thermodynamic equilibrium modelling (TEM)

TEM is a well-established method to investigate gasification. The equilibrium models are typically based on the Gibbs free energy minimization (GFEM) principle and are simpler than other mathematical models, making them an essential tool in understanding the gasification phenomenon through parametric studies. The TEM studies used HSC Chemistry software for prediction of equilibrium composition of the BCLG reactions. Furthermore, the studies evaluated different biomass/char for their reactivity and thermodynamically optimised BCLG reactor conditions. Relevant TEM for BCLG are summarised in Table 4.

Table 4
Summary and discussion of TEM for BCLG.

Authors (Year)	OC(s)	Remarks
Huang et al. [61] (2013)	Natural hematite	(i) Studied the equilibrium compositions of the BCLG reactions (ii) Verified the modelling results using experimental studies conducted in a BFB reactor and reported consistency of the modelling predictions with experimental data
Huang et al. [65] (2015)	Fe ₂ O ₃	(i) Examined the biomass char reactivity with as OC under different atmospheres using TEM(ii) Reported that despite the complete depletion of lattice oxygen, the CCE registered was only 40.80 % at 1000 °C under inert conditions
Ran et al. [82] (2016)	CuO/MgAl ₂ O ₄	(i) Evaluated use of OC in BCLG integrated with oxygen uncoupling(ii) Optimized the effect of CuO-to-carbon molar ratio on the product gas composition and reported the optimal CuO/C ratio as 0.35
Huang et al. [62] (2017)	NiFe ₂ O ₄	(i) Investigated the use of as OC and biomass char as fuel in BCLG(ii) Determined optimal ratio of OC-to-char for maximum CGE as 0.3
Yang et al. [144] (2021)	Waste-carbide slag	(i) Studied the feasibility of using as OC, hydrogen carrier, and in-situ carbon capture using lignite in the BCLG process.(ii) Reported optimal temperature range of 350–627 °C and suitable C:Ca(OH) ₂ M ratio greater than 1:4 for high H ₂ production and in-situ carbon capture.(iii) Lower reaction pressure of 0.1 atm was observed more favorable for BCLG of lignite.

4.2. Process modelling

Although thermodynamic equilibrium models can undoubtedly predict the product compositions and give insight into the reactor

behaviour, process modelling enables us to understand the integrated process performance. In multiple studies, ASPEN software tool was used to simulate the two reactors (fuel and air reactor) simultaneously and integrate downstream processes such as electricity generation, product gas cleaning, and conditioning. In these studies, a detailed techno-economic analysis of BCLG was conducted and compared it with existing combustion and gasification technologies. Based on the studies examined, it can be concluded that BCLG is an economical option with a lower operational cost and higher overall process efficiency. Table 5 summarises the process modelling studies and highlights important observations.

4.3. Kinetic modelling

Kinetic modelling aims at elucidating the reaction kinetics, which provides essential information about the reactions, thereby assisting in the numerical optimisation of the reactors. Furthermore, such studies help to evaluate the role of operational parameters on system efficiency and performance.

Although the reaction mechanism of BCLG is complex and the exact mechanism is yet to be determined, previous research has focused their kinetic investigations on the reactions in the fuel reactor (see Table 1). In addition, some of these studies have validated their numerical simulations with experiments conducted using TGA with temperatures ranging from 25 °C to 1250 °C. Selected kinetic studies are presented in Table 6.

Taking into account the findings from these studies and others, and considering the reaction pathway of BCLG reactions discussed in section 2.1, reactions taking place in the fuel reactor can be divided into three fragments: biomass pyrolysis, gas–solid interactions between gaseous volatiles/solid OCs, and solid–solid interactions between solid char/solid OCs. Typically, the shrinking core model investigates the kinetics of biomass pyrolysis and gas–solid reactions [21,149]. Initially, the model considers the reactions on the biomass particle surface followed by the release of volatiles from the particle surface and, finally, the

Table 5
Process modelling studies reported for BCLG.

Author (Year)	Feedstocks	OC(s)	Unit capacity	Observation(s)	Important result(s)
Aghabaranjad et al. [59] (2010)	Biomass*	Co ₃ O ₄ /Al ₂ O ₃	85 tons/day (330 operational days/annum)	System (CAPEX/annual OPEX):CGPO (6.3 million USD/1.9 million USD) ;CG (8.5 million USD/1.14 million USD) ;BCLG (9.7 million USD/1.32 million USD)	BCLG is economically feasible with lower OPEX than conventional gasification systems
Li et al. [47] (2010)	Poplar (@50 % MC)	Fe ₂ O ₃	36 tonne/h @50 % MC	η _{process} (H ₂ production and electricity generation): 75 % and 38 %	Process efficiency 10–25 % higher than conventional biomass combustion and gasification systems
Gopaul et al. [60] (2014)	Poultry litter	Fe ₃ O ₄ , CaO	1 kmol/h	(i) System 1: CaO (OC), 0.79 kmol/kmol PL (syngas yield), 93 mol% (H ₂ -concentration)(ii) System 2: Fe ₃ O ₄ (OC), 2.54 kmol/kmol PL (syngas yield), 63 mol% (H ₂ -concentration)	Higher H ₂ concentration using CaO as OC due to adsorption of CO ₂ by CaO
Kuo et al. [145] (2018)	Raw and torrefied wood	Fe ₂ O ₃	10,000 kg/h	(i) Unit 1: Raw wood (feed), 56.7 % (η _{H₂-production}), 4.5 % (η _{electricity}), 61.2 % (η _{overall}), 117.6 g H ₂ /kg-feed (ii) Unit 2: Torrefied wood (feed), 61.4 % (η _{H₂-production}), 4.6 % (η _{electricity}), 66.0 % (η _{overall}), 143.5 g H ₂ /kg-feed η _{power} : 33.51 %, Gas turbine efficiency: 33.24 %, Steam turbine efficiency: 34.01 % (iv) η _{power} of existing demonstration plant in China: 30–32 % (26–46 t/h capacity)	Torrefied wood performed better in terms of H ₂ production efficiency, H ₂ yield and overall efficiency. However, electricity generation efficiency was similar to raw wood due to greater energy requirements for steam generation.
Ge et al. [38] (2019)	Rice straw	Hematite	30 ton/h	η _{power} : 33.51 %, Gas turbine efficiency: 33.24 %, Steam turbine efficiency: 34.01 % (iv) η _{power} of existing demonstration plant in China: 30–32 % (26–46 t/h capacity)	BIGCC-CLG unit offers higher power efficiency than existing IGCC demonstration units.
Dieringer et al. [25] (2020)	Wood pellet	Ilmenite	1 MWth input	(i) Two simulation approaches: (a) diluting OC with an inert heat carrier and (b) restricting airflow to the air reactor (iii) CGE: 72.5–77.1 % (under autothermal conditions, SBR: 0.9–0.3)	Heat and oxygen transport de-coupling is necessary. Limiting oxygen supply to fuel reactor is an essential factor in increasing CGE

Notes: *Biomass composition – 48 wt% C, 6.2 wt% H, 0.2 wt% N, 0.6 wt% S, 45 wt% O.

Table 6
Summary of BCLG kinetic modelling studies.

Authors (Year)	Feedstock OC	Temperature (°C)	Activation energy (kJ/mol)	Important kinetic model(s)
Huang et al. [62] (2017)	Biomass char NiFe ₂ O ₄	30–1250	E = 20.38–568.9	24 models (RNSGM, CRM)
Hu et al. [146] (2018)	Microalgae Fe ₂ O ₃	30–1100	E _{HM} = 11.7–46.5 E _{SCM} = 2.8–43.7	HM, SCM
Yan et al. [147] (2020)	Corn straw Fe ₂ O ₃ / Al ₂ O ₃	50–1100	E = 82.5–104.9	30 models (RNSGM, PBRM, CRM)
Li et al. [148] (2020)	Graphite CaFe ₂ O ₄	27–1200	E = 306–600	13 models (CRM, 1D, 2D&3D diffusion)
Lin et al. [93] (2020)	Pine NiFe ₂ O ₄	25/120–950	E _{DAEM} = 100–350	DAEM

released volatiles reacting with the lattice oxygen on the OC's surface. During these steps, the model assumes that the biomass and OC particles shrink due to devolatilisation and oxygen consumption, respectively. In addition, the gas–solid interactions can be studied using the chemical reaction model [147,150]. Furthermore, the subsequent growth, random nucleation method, and modified random pore model are used to study the solid–solid reactions occurring between char and OC [62,110,151,152]. The first two models assume that biomass char reacts with the OC on its surface, resulting in char gasification and deposition of the char residue on the OC. In the last model, pores between overlap and expansion compete with each other, which dictates the solid–solid reaction rate [152,153]. In the BCLG reactor, the above-mentioned interactions occur simultaneously, which adds to the process complexity. Therefore, it is imperative to consider the reaction kinetics to design a reactor successfully.

5. Process challenges and technological aspects for industrial application

Significant challenges in the design and operation of BCLG arise due to the dynamic nature of the process and the complexity of the numerous reactions and interactions between solids and gases. In addition, considering the scale-up of BCLG technology, several issues need to be addressed before implementing the technology on a commercial scale.

5.1. Development of OCs

Among the many challenges, the development of OCs poses a significant challenge. In general, the longevity of OCs, unstable cyclic performance, agglomeration and attrition behaviour, carbon deposition, their degradation, high solid inventory, environment friendliness, and economics pose a significant challenge towards achieving higher process efficiencies. Consequently, optimizing the OC composition and reactor system operating conditions can improve the lifetime and cyclic performance of the OC carrier particles. The adopted OC must be adequately reactive with a reasonable lifetime, economically viable, and environmentally justifiable so that the BCLG technology can be implemented at a commercial scale.

In a real reactor system, solid attrition can reduce the lifetime of OCs. Physical attrition can happen due to abrasion and erosion of OC particles in the fluidized bed reactors. Consequently, it affects the operation as a supplementary stream of OC is required to compensate for the loss, directly causing a significant increase in operational cost. Therefore, waste-type OC materials can provide a cheap alternative to replace the

worn OC material. However, it becomes difficult to attain an acceptable balance between the OC cost and performance as they are positively correlated. Here it is noteworthy that the actual OC cost should collectively account for the raw material price, preparation cost, and cost in terms of life cycle, use of waste materials, and environmental impact [1]. Admittedly, the actual costs of synthetic OCs are less competitive than the natural ores (e.g., hematite, bauxite and ilmenite) or industrial wastes (e.g., LD slag, red mud and copper slag). Previous studies have indicated that natural ores or industrial waste suffer from relatively low reactivity compared to synthetic OCs. Another alternative could be to use molecular sieve-encapsulated OC materials with high stability, strength, activity and longer lifespan. However, better reactivity can also be achieved by mixing low-cost materials or using smaller quantities of support materials. Therefore, simple, low-cost and adequate particle mixing and preparation methods are needed. Hence, considering a good compromise between the actual cost and reactivity, natural ores or industrial wastes can be potentially considered as a feasible option for OC materials.

5.2. Impact of biomass ash

The use of high-ash-containing biomass in the BCLG process poses a significant concern due to the inorganic matter present in bottom ash, which gets deposited and interacts with OC to form agglomerates [154,155]. The formation of agglomerates that significantly increase the OC diameter can change the fluid dynamic properties of the system, thereby affecting their fluidisation and eventually leading to operational problems [156]. On this basis, one may conclude that the recovery cycle of agglomerated OC would require more residence time than normal, which may not be affordable in the air reactor. This can result in maloperation and lowering the quality of product. Consequently, it is essential to drain the bottom ash periodically, thereby prolonging the lifetime of OC [157]. Therefore, it becomes important to consider an easy way for OC particles separation from ash using rotating fluidised beds or magnetic separation.

5.3. Reactor development

The know-how and experiences from circulating fluidised bed systems are essential for developing the BCLG reactor; however, thermal integration and heat management issues between the two reactors pose significant challenges to its design [157,158]. The endothermicity of the fuel reactor requires the air reactor to operate at higher temperatures and supply thermal energy via circulating OC particles. Therefore, maintaining optimum temperatures in both the reactors mainly depends on the solid circulation rate and OC properties. In addition, high solid circulation rates are necessary to prevent large temperature drops, whilst increasing the circulation rates can significantly increase the temperatures in the air reactor leading to the problem of OC agglomeration (e.g., OCs containing copper can easily form agglomerates due to their low melting point).

Furthermore, the issue with high solid inventory can potentially be a big problem in the actual operation of the BCLG process with an interconnected fluidised bed reactor system. More specifically, higher circulation rates require additional energy, directly affecting the system's energy efficiency. Consequently, adoption of an OC is needed that can thermally stabilize the overall process, and such an OC can be a mixture of different metal oxides. Moreover adopting a mixture of metal oxides can add to their bi-functionality of improved catalytic activity alongside maintaining good thermal stability.

It is imperative to study the residence time distribution of OC particles in the BCLG system as it influences both the design and the operation of the reactors. Since oxygen travels with solid materials, it is expected to have slow reaction rates and thus longer residence times. Consequently, it can lead to a lower capacity of reactors. To the best of our knowledge, the impact of residence time has rarely been considered

during the development of BCLG reactors. We can overcome such challenges and better optimise the BCLG process by investigating and optimising the effect of different residence times using mathematical modelling. Additionally, the residence times in a fluidised bed reactor can be altered physically by modifying the reactor aspect ratio and reactor exit and adding baffles or stages.

To date, majority of the BCLG experimental studies have been conducted in bench-top reactors under idealised conditions, which essentially cannot mimic industrial-scale applications. One may conclude that multiplicities of outstanding challenges, partly outlined above, call for continuous experimental approaches using actual conditions to understand the system behaviour better and overcome practical technological challenges.

5.4. Mathematical modelling

In order to establish optimal reaction parameters for stable operation in a longer term, it is highly desired to explore more sophisticated mathematical modelling studies, including thermodynamic, kinetic, and process simulation studies.

Although the TEM approach is valuable in understanding and predicting the thermodynamic limits of BCLG, its reliability has been an issue. This is because the TEM approach assumes that the participating components react in a thoroughly mixed steady-state condition having infinite residence time, uniform temperature and perfect mixing. However, the assumption holds reasonable when the components' residence time in the reactor is longer than the reactants' half-life, have an almost perfect chemical mixing, and temperature can be assumed to be constant [159]. Unfortunately, such conditions can mostly be met in specific reactors, such as downdraft fixed-bed gasifiers, with temperatures higher than 1200 °C [160]. Additionally, the models can predict unrealistic components due to misleading or inappropriate data selection [161]. Nonetheless, the accuracy of thermodynamic equilibrium models can be improved by comparing the simulation results with experimental data and modifying the models by using appropriate factors/coefficients/databases and carefully selecting input conditions. Therefore, none of the discussed research work adapted calibrated/constrained TEM for BCLG, thereby creating opportunities for further exploration.

To date, investigations on the internal and external diffusion mechanism and behaviours of gasification agents during char gasification are insufficient. Additionally, the diffusion and interaction mechanism of generated volatiles and gasification agents on OC surfaces are limited. Therefore, further modelling studies are needed to examine the mass transfer mechanism and comprehend its resistance at the particle level for varying degrees of conversion. Furthermore, metal slags used as OC can affect the gasification performance due to the presence of impurities such as silica, magnesium, phosphorous, potassium, zinc and calcium. Such impurities can inhibit/promote the activity of OC materials, thereby altering the phase equilibrium and influencing the overall gasification performance. To enable the operation of BCLG at a commercial scale, further investigations are needed to comprehend the impact of such impurities.

Apart from technical investigations, the economic and environmental assessments of BCLG technology are still limited and primarily include the use of pure OC materials. With regard to economic evaluations, this should be examined using different metal slags as OCs in BCLG and compared to conventional gasification processes. From the environmental perspective, life cycle analysis needs to be addressed, specifically using recycled CO₂ as a gasification agent.

6. Perspectives on BCLG as a decarbonized circular economy technology

6.1. Negative emissions

Undoubtedly, the BCLG process holds a great potential to produce

high-quality syngas, H₂, or liquid biofuels (via Fischer-Tropsch synthesis). Additionally, BCLG process can effectively achieve negative emissions since the fuel reactor generates CO₂ in a relatively concentrated form, making the BCLG process appropriate for CO₂ separation and utilisation. In particular, a study suggested that utilising recycled CO₂ as a gasification agent provides a more economical option than steam as it reduces the energy consumption used for steam generation [162]. Furthermore, no evident difference was highlighted in the predicted gas concentrations when using steam and CO₂ as gasification agents. Another study examined the effect of using CO₂ in the BCLG process with Fe-based OC [163]. It was concluded that the coexistence of CO₂ and OC displayed a synergistic effect on tar cracking. CO₂ promoted heavy tar cracking while OC reduced light tar production. Although minimal studies are present on recycled CO₂ utilisation in the BCLG process, several studies indicate the potential realisation of CO₂ gasification, thereby pointing to a future scenario of recycling a CO₂ stream to the fuel reactor and minimising CO₂ emissions [164–169].

Several studies recommend using CO₂ as a biomass gasification agent as it offers numerous advantages [167,169–173], such as (i) a less corrosive gasification medium than steam, (ii) improved gasification output yield and efficiency, and reduced char residue by generating a more reactive char, and (iii) flexibility in syngas production, thereby opening avenues for multiple downstream applications. Multiple studies were performed to understand the gasification reaction behaviour in a pure CO₂ atmosphere [165,174–176] or an eclectic atmosphere with multiple CO₂ concentrations [177,178]. Furthermore, some authors presented results from experimental studies of CO₂ gasification with different feedstocks, including biomass char [179], wheat straw char [180], paper and cardboard [166], oil palm shell char [181], and olive residue [182]. However, a majority of the CO₂ gasification studies were limited to lab-scale and optimized reactor conditions using CO₂ at commercial scale are not well established. Most of the experimental studies were conducted using CO₂ with nearly 100 % purity. It may not be practical at the commercial scale due to the presence of impurities such as H₂O, SO_x, NO_x, NH₃, light/heavy hydrocarbons, H₂S, N₂ and CH₄ in recycled CO₂ stream [183–185]. These impurities can potentially alter the phase equilibrium, thereby affecting the activity of OCs and gasification performance. Therefore, fundamental and technical knowledge of CO₂ gasification needs to be further explored.

Moreover, emissions of gaseous pollutants and their precursors (e.g., NO_x, HCN, NH₃, SO₂) were significantly lower in BCLG than those in conventional biomass gasification [66,130]. It can be argued that during the BCLG process, fuel does not come in direct contact with N₂-rich air, thereby avoiding N-based emissions [186]. Additionally, due to very low oxygen partial pressure in the fuel reactor, the preliminary products of nitrogen (NH₃ and HCN) will not oxidise to generate NO_x. Furthermore, a research investigated the role of red mud (Fe-based OC) in reducing air pollutant emissions (e.g., HCN, NH₃, NO, SO₂) [66]. Interestingly, the authors observed that the peak values of the emissions decreased with the increase in the Fe₂O₃-to-fuel ratio and ascribed the decrease to the presence of alkaline components (Na₂O and CaO). Their results were in agreement with another study [187]. A different study explored the nitrogen changes and migration (N-Gas, N-Tar, and N-Char) due to the presence of OC (copper slag modified by NiO) during BCLG of sewage sludge [186]. The nitrogen migration route is shown in Fig. 11. It was concluded that the increase in OC promoted oxidation and catalytic cracking of NO_x precursors (N-NH₃ and N-HCN), thereby significantly increasing the N₂ yield and decreasing NO_x emissions.

Therefore, OC capability is not limited to providing oxygen and transferring heat. Additionally, it plays a crucial role in abatement of emissions such as NO_x, HCN, NH₃, SO₂ and CO₂. Apart from reactivity, mechanical properties, cost and environmental friendliness, the selection of suitable OC material should also consider its characteristics to absorb/reduce particular pollutants.

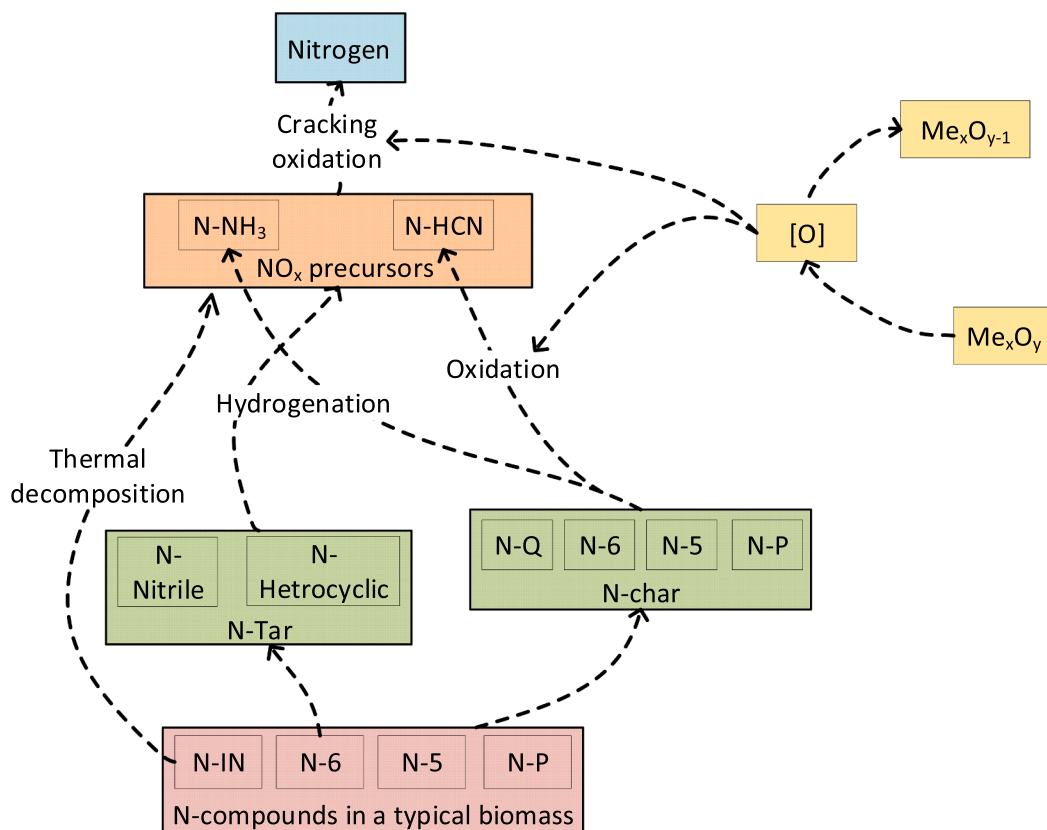


Fig. 11. Nitrogen migration route in BCLG [186]. Note: N-IN, N-6, N-5 and N-P refers to inorganic ammonium nitrogen, pyridine nitrogen, pyrrole nitrogen and protein nitrogen, respectively.

6.2. Circular economy

The concept of a circular economy addresses current sustainability issues while creating value from the environmental, societal, and economic outlooks. One of the keystones of this concept lies in designing circular pathways for the products usually ending up as waste. Besides the capability of BCLG to produce high-quality biofuels and achieve negative emissions, it can also contribute to the circular economy by utilising waste materials. To complement this, several studies have investigated the use of waste streams such as sewage sludge [74,76], food waste [101], and agricultural and forest residues [29,63,78,79] in the BCLG process. Additionally, multiple research studies successfully demonstrated the use of industrial waste such as LD slag [102], copper slag [76], petrochemical sludge [79], and red mud [101,188] as OCs in the BCLG process. The results from using waste materials for BCLG were discussed in detail in previous sections.

7. Conclusion

BCLG is a promising energy technology that could efficiently convert biomass into high-quality syngas to realize decarbonised circularity. Compared to conventional thermochemical processes, BCLG offers negative equivalent CO₂ emissions (-14.58 kg-CO₂e/kg-H₂) with a lower H₂ production cost of 3.37 USD/ kg-H₂, however, it is still under development with a TRL of 3 to 5. Thus, this review extensively updated experimental research related to BCLG in terms of optimisation of process parameters (e.g., temperature, gasification agent, and OCs), selection and modification of OCs, and reactor design in order to enhance the carbon conversion efficiency and improve the quality of produced syngas. Moreover, the properties of OCs have been holistically analysed from technological, economic, and environmental perspectives in order to screen appropriate and affordable OCs for BCLG (e.g., Fe-OC). On the

other hand, thermodynamic, process and kinetic modelling studies are systematically summarised to further optimize BCLG and design the reactor. This review indicates constrained thermodynamic modelling would be developed for BCLG, while more efforts should be devoted to investigations on internal and external diffusion mechanisms, and influences of volatiles and gasification agents on OC and char gasification. More importantly, perspectives on negative emissions and circular economy are provided to address the potential challenges in industrial application. In particular, affordable OCs with acceptable reactivity would be developed from natural ores and industrial waste slags. Minimizing the impact of biomass ash on OCs through easier and efficient separation is also proposed. Ultimately, combined mathematical modelling and continuous reactor development is essential to shed light on scaling-up application of BCLG.

CRediT authorship contribution statement

Avishek Goel: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Visualization, Writing – original draft. **Elyas M. Moghaddam:** Conceptualization, Methodology, Validation, Visualization, Writing – review & editing. **Wen Liu:** Investigation, Methodology, Writing – review & editing. **Chao He:** Conceptualization, Methodology, Project administration, Funding acquisition, Resources, Supervision, Validation, Visualization, Writing – review & editing. **Jukka Konttinen:** Conceptualization, Methodology, Project administration, Resources, Supervision, Funding acquisition, Project administration, Validation, Visualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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