

Engineering thermochemistry to cope with challenges in carbon neutrality

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ARTICLE INFO

Handling Editor: Jin-Kuk Kim

Keywords:

Engineering thermochemistry
Energy utilization
CO₂ emission
Thermochemical reactions
Carbon super-emitters

ABSTRACT

More than 90% of anthropogenic carbon emissions are from uses of organic carbon resources and carbonate minerals that cannot be abandoned any time soon. In this context, we have realized that the most effective strategy to cope with carbon-neutral challenges is to focus on a few super-emitters, which are all associated with heat-induced or heat-driven thermochemical reactions. To assist in reducing CO₂ emissions from these super-emitters, we introduce an emerging interdisciplinary Engineering Thermochemistry (ETC) that focuses on heat-induced/driven thermochemical reactions and their engineering. Combined with some exemplary processes, we demonstrate how and why ETC can play a vital role in innovating CO₂ super-emitting processes to reduce energy consumption and carbon emissions substantially at the scale of several billion tons. The approaches discussed in this study can help governments and researchers to establish applicable policies and develop practical techniques to meet the challenges of CO₂ emission reductions toward a green and carbon-neutral future.

1. Introduction

Transformation to carbon neutrality is a globally profound economic and social challenge, which has already had and will continue to have significant effects on all aspects of our human life (He et al., 2013). As perhaps the greatest challenge of this century, carbon neutrality requires reductions of net annual carbon dioxide emissions from approximately 20 billion tons (Friedlingstein et al., 2020; Hepburn et al., 2019) to zero by 2060. To achieve this ambitious goal, many nations have committed unprecedented efforts, despite the challenges they face in balancing carbon reduction with economic growth and social development. Given the magnitude of carbon emission reductions in such a short time frame, there is an urgent need to identify significant emission sources and take targeted mitigation strategies.

1.1. Fossil energy consumption and carbon emissions

In principle, almost all human activities produce carbon dioxide directly or indirectly. Statistically, over 80% of the world's primary

energy consumption is fossil fuels, contributing to approximately 90% of global carbon emissions (see Fig. 1) (BP, 2023; IEA, 2022). This is particularly true in countries such as China, India, Vietnam, Indonesia, Australia, and South Africa, where carbon-intensive coal and oil take the lion's share of the energy supply to support economic growth and social development (BP, 2023). In China, coal has been the dominant energy source, which accounts for 55–80% of the total primary energy consumption (Fig. 2(a)). It is worth noting that the proportion of coal consumption in total primary energy seems to have a downward trend in recent years, but its absolute quantity has increased rapidly in the past two decades and remained stable or even increased recently (Fig. 2(a)). Consequently, almost all of China's CO₂ emissions come from the use of fossil fuels (Fig. 2(b)).

1.2. Renewables not quick fixes

Undoubtedly, the ideal way to achieve global carbon neutrality is to replace all fossil fuels and materials with renewable ones. However, the reality is that renewable energy (e.g., solar, wind, hydro, and biomass)

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<https://doi.org/10.1016/j.jclepro.2023.137943>

Received 28 April 2023; Received in revised form 26 June 2023; Accepted 27 June 2023

Available online 28 June 2023

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supplies only 18% of the world's energy consumption, although renewable energy generation reached an all-time high in 2021 (BP, 2023). It has to be admitted that it is hardly plausible for renewable energy to become sufficient enough to allow a complete phase-out of fossil fuels in the foreseeable future, not to mention that many renewable technologies and infrastructures are far from mature. A real risk is that it will be unable to provide renewable energy on the scale, stability, and economy needed to replace fossil fuels in the committed carbon-neutral time.

Recent geopolitical conflicts have caused energy shortages in some European countries, such as Germany, Britain, and France. As a result, these and other affected countries, such as Japan, South Korea, India, and many others, have been forced to quietly or publicly revise their longstanding policies of abandoning coal energy supplies. In fact, these countries have recently been increasing their coal-fired power generation capacity to make up for the energy supply shortage caused by the uncertainty and instability in the supply of natural gas and renewable energy (Hinweis, 2022; MercoPress, 2022). Due partially to geopolitical conflicts, the recent shortage in energy supplies and the surge in natural gas prices has forced some of the power plants that switched from coal-firing to gas-firing a few years ago to change back to coal recently in the United States and Europe where competition between gas- and coal-fired power plants is tightest. As a result, CO₂ emissions from coal-fired plants jumped by 17% and 16% in the United States and the European Union in 2021, respectively. In other parts of the world, we expect that fossil energy consumption is very likely to maintain or even raise its dominant role in energy supply for a long time in the future, considering especially the imbalance in energy resources and the inequality of economic development between countries and regions. Surely, as far as carbon neutrality is concerned, renewables will be the ultimate solution, but the reality is that they are not quick fixes. Fossil energy, especially coal, once widely shunned around the world, is far from being able to fade away when resources, geographic, and geopolitical realities are concerned (Steckel and Jakob, 2022). Therefore, we must recognize and acknowledge that we must deal with fossils for years to come while making all our best efforts to curb carbon emissions.

1.3. CO₂ super-emitters

In the face of the reality mentioned above, it is vital to identify the strategies and technical routes to curb CO₂ emissions from fossil-related sources effectively and quickly. While policymakers are bringing in legislation to combat climate change, scientists worldwide have proposed various technologies and pathways to reduce CO₂ emissions (Bharath et al., 2023; Bruckner et al., 2022; Govindan et al., 2022;

Hepburn et al., 2019; Jin et al., 2022). However, it seems that not enough attention has been paid to how to curb carbon emissions more effectively and quickly at meaningful scales (e.g., billions of tons of CO₂ reductions) with the least resources and costs while being able to continue to improve the quality of life.

Statistic data shows that most CO₂ emissions are from four industrial sectors, including electric power and heat generation, ferrous metals and non-ferrous minerals processing, and transportation (Fig. 3(a)). By comparison, CO₂ emissions from other sectors, such as petrochemical and chemical industries, and urban and rural activities, are far less significant. An in-depth analysis indicates that a small number of super-emitters are actually responsible for a disproportionately large share of the emissions. In China, these super-emitters are the following (Fig. 3 (b)): 1) coal-fired power plants for electricity generation, 2) coal-fired boilers and furnaces for residential, commercial, and industrial steam/hot water production and heating, 3) iron and steel making, 4) non-ferrous metallurgical processes, 5) cement production, and 6) lime production (Xu et al., 2022). All these processes emit over 90% of China's CO₂ emissions of 10.5 billion tons. Adapting to this reality, it is rational to believe that carbon neutrality can only be attained effectively, cost-effectively, and quickly by focusing on reducing CO₂ emissions at sources from these super-emitters.

A further examination of the super-emitters listed in Fig. 3(b) reveals that all these processes involve heat-induced or heat-driven thermochemical reactions (such as combustion, decomposition, calcination, reduction, and sintering) that are practiced in a wide range of industrial fields (i.e., from energy to ferrous/non-ferrous metal smelting and production as well as others) to produce electricity, heat, power, materials, and other products essential to our life. These thermochemical processes can be classified into three categories.

- Coal-fired combustion processes, including coal-fired electric power generation, district/industrial heating, and rural household cooking and heating (Zhao et al., 2017)
- Electricity-heating processes, including electrolytic (e.g., aluminum electrolysis), ferrous (e.g., pig iron), and non-ferrous (e.g., metallurgical silicon, ferrosilicon, ferromanganese, ferrochrome, tungsten iron, silicomanganese) smelting (Lin and Xu, 2015; Mi et al., 2014)
- High-temperature thermal processes, including production processes of cement and lime using chunk-sized feedstocks, generally in rotary/shaft kilns (Mikulčić et al., 2016; Mousa et al., 2016; Nie et al., 2022; Shahin et al., 2016; Zhang et al., 2022).

Despite being distributed in different industries, the CO₂ super-emitters are all, not surprisingly, energy-intensive and involve heat-

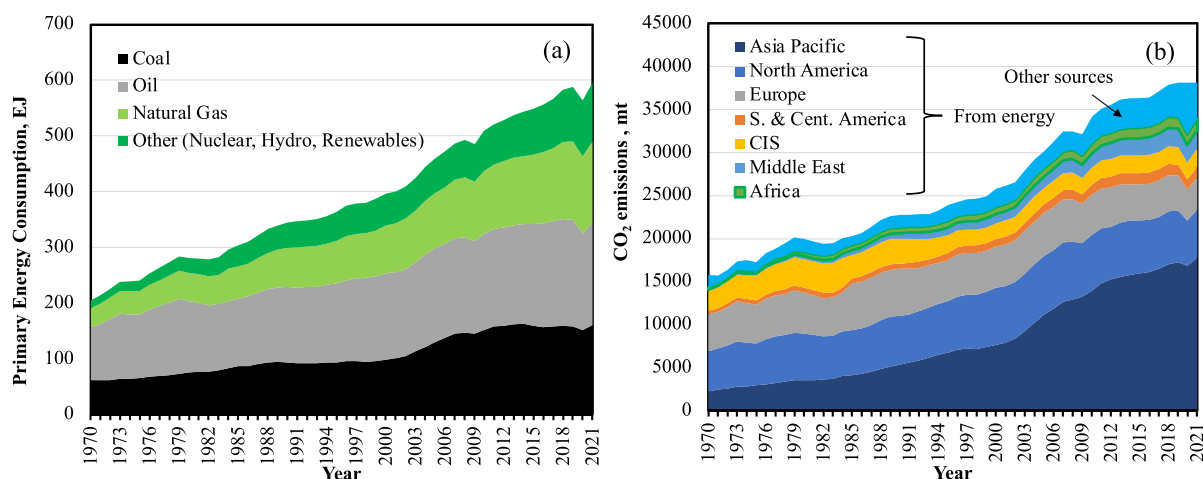


Fig. 1. (a) World primary energy consumption and (b) CO₂ emissions (BP, 2023; IEA, 2022).

induced or heat-driven thermochemical reactions. In terms of average primary energy utilization efficiency, coal-fired power generation is about 40%; coal-fired industrial boilers are about 65%; electric processes are less than 20%; high-temperature electric heating processes are less than 50%. Doubtlessly, there is still much room for technical improvement and carbon reductions with regard to such thermochemical processes.

1.4. The objectives of this work

In the context of reducing CO₂ emissions, we have recognized the need for unprecedented scientific innovation and technological breakthroughs targeting the thermochemical reactions involved in the preceding CO₂ super-emitting processes. Given the unique characteristics of the diverse industrial sectors, it is indisputable that we need a scientific discipline to deal with common scientific problems and engineering issues existing in thermochemical industries, thereby promoting the research, innovation, and engineering applications of involved thermochemical reactions.

In response to such a need, Engineering Thermochemistry (ETC) has emerged as an interdisciplinary scientific and technological field that studies and engineers heat-induced/heat-driven thermochemical reactions. In this study, we begin with introducing the concept of ETC, covering its conceptual initiation and the essential principles. After a brief analysis of the characteristics of the CO₂ super-emitters, we focus on discussions of potential techniques or alternative thermochemical reactions to reduce CO₂ emissions from the super-emitting processes effectively and economically. We acknowledge that there are numerous technological solutions and strategic pathways that have been proposed and discussed publicly on various occasions to achieve carbon neutrality, such as renewable energy, carbon capture, utilization, and storage (CCUS), our efforts in this study are, however, devoted solely to demonstrating how ETC can help advance super-emitting thermochemical reactions. To achieve this goal, some innovative reaction processes and reactor designs are exemplified to show their potential in CO₂ emission reductions, which are estimated approximations based on specific assumptions.

2. Engineering thermochemistry

2.1. The initiation of the concept

Heat-induced and/or heat-driven thermochemical reactions are a particular class of chemical reactions that generally occur at high temperatures without catalysts (except in some specific cases). Statistically, as high as 80% of industrialized chemical reactions are heat-induced and/or heat-driven thermochemical reactions. Typically, such reactions include pyrolysis, coking, carbonization, gasification, combustion, decomposition, calcination, thermal oxidation, thermal reduction, thermal cracking, and sintering of various solid materials. Some of these reactions have been discovered and utilized for centuries in a wide array of industries, such as chemical, energy, material, environmental, metallurgical, mechanical, and many others. In these industries, thermochemical reactions are often used to transform fossils and natural resources into final products or intermediate materials to be further processed by their subsequent catalytic, photochemical, and electrochemical reactions.

Despite the scientific importance and industrial popularity, no scientific discipline focuses on the science and technology of heat-induced and/or heat-driven thermochemical reactions. Consequently, it is not uncommon to encounter obstacles and contradictions in exchanging the related knowledge and experience between practitioners in different processing industries and scientists from various narrow scientific disciplinary backgrounds. Omitting the interdisciplinarity of heat-induced and/or heat-driven thermochemical reactions makes innovations of these reactions very difficult, thereby significantly limiting their capacity and potential to produce energy and materials essential for developing green and sustainable industries and societies. It is evident that interdisciplinary thinking and approaches are required to reform research and innovation of thermochemical reactions because the integrative thrust goes beyond the mere concatenation of contributions from narrow individual disciplines.

In this context, Chinese scholars have proposed the concept of Engineering Thermochemistry as an interdisciplinary and cross-industrial scientific discipline (Xu, 2019; Xu et al., 2022). Focusing specifically on heat-induced/-driven thermochemical reactions, ETC refines and resolves their common scientific fundamentals and engineering issues, thereby promoting the discovery, research, innovation, and engineering

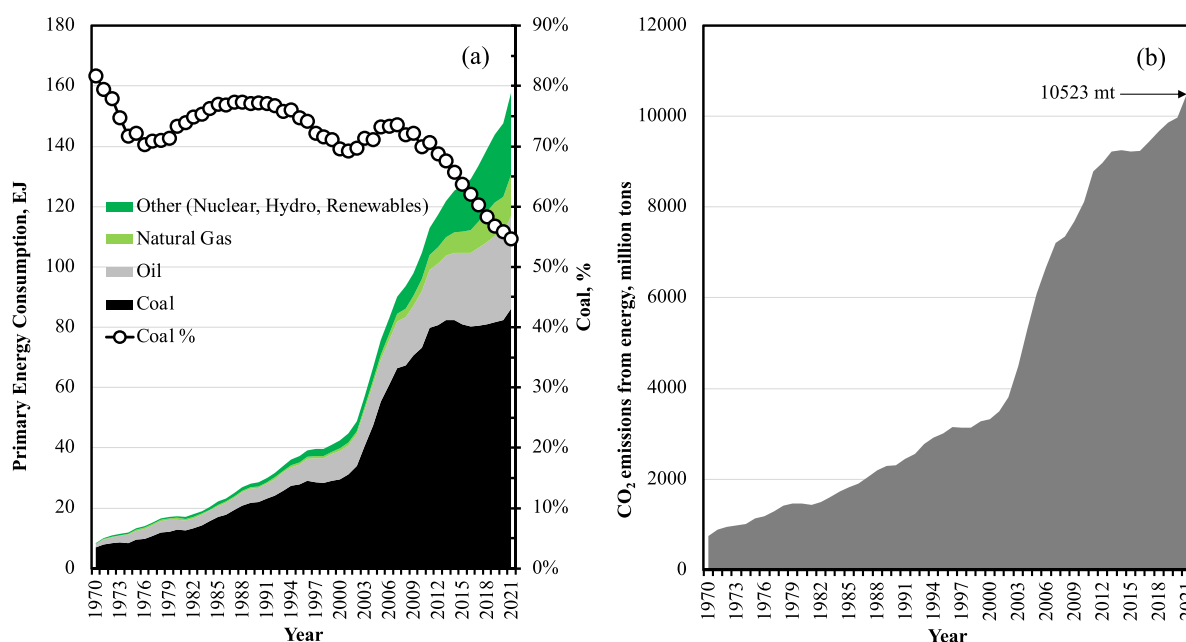


Fig. 2. (a) China's primary energy consumption and (b) CO₂ emissions (BP, 2023).

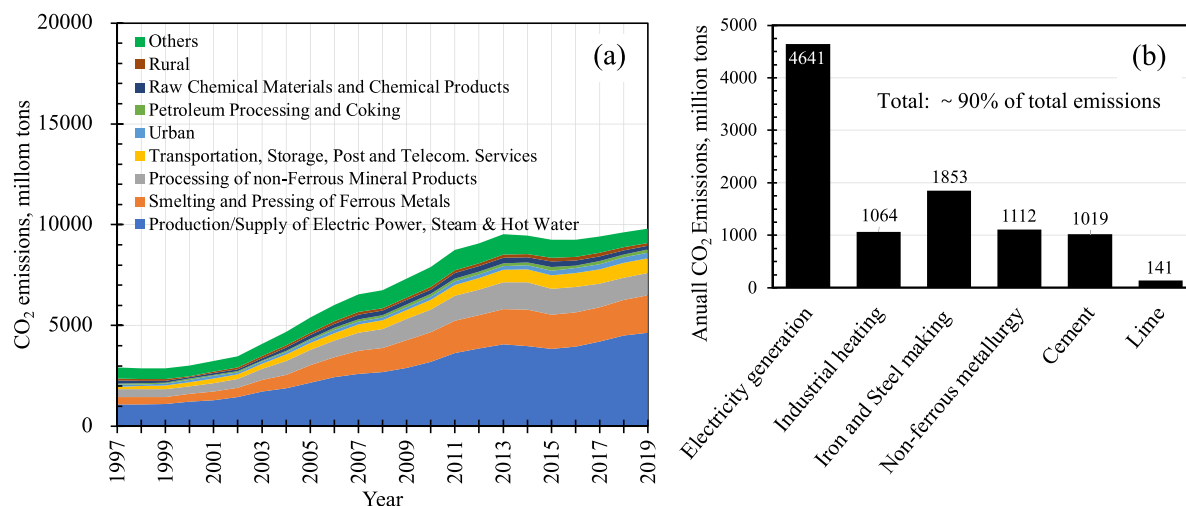


Fig. 3. China's CO₂ emissions from major industries in 2020 (Shan et al., 2016, 2018, 2019, 2020; Zhou et al., 2022).

of thermochemical reactions in a scientific and systematic approach (Fig. 4).

2.2. The essential context of ETC

In laboratories, thermochemical reactions are often investigated by means of their chemistry to understand the structure of substances, how they react when combined or in contact with one another, and how they behave under different reaction conditions. In principle, it must be thermodynamically feasible for a thermochemical reaction to occur, which is determined by thermochemistry, a branch of chemistry. Thermochemistry is also used for calculating energy changes and predicting product profiles at thermal equilibrium states. In practice, for a thermochemical reaction to be industrially valuable, it must also be feasible kinetically, i.e., the reaction rate is fast and the product is selective.

For this reason, it is necessary to investigate reaction science and applied chemistry, including reaction mechanisms and kinetics, in order to provide an in-depth understanding of reaction schemes, intermediary products, competing reaction schemes, reactant conversion, product selectivity, and reaction rate under various influencing factors or conditions. These investigations are conducted generally in ideally configured laboratory reactors (such as isothermal/non-isothermal differential and lab-scale reactors with negligible effects of fluid flow and mass/heat transfer on the reaction performance) and well-controlled reaction conditions (e.g., uniform reaction temperature and time, ideal fluid flow pattern, preferred solids flow and mixing, and no reactor geometric effect). With the information gained from these investigations, it is

possible to implement thermochemical reactions in practical industrial processes. However, the industrial implementation process is challenging because, in most cases, there are gaps or missed links between chemistry fundamentals and practical applications. For example, there is often a mismatch between fundamental research and practical applications regarding reactor configurations, reaction conditions, fluid dynamics, temperature profiles, and heat transfer.

ETC is initially proposed to link and integrate the fundamental research and engineering of thermochemical reactions in different disciplines and industries. After several years of development, it has emerged as a new scientific discipline and connotes more specialization of scientific significance. It discerns and integrates a common set of core metaphors and concepts in the field of fundamental research and engineering technologies of thermochemical reactions that used to be dealt with separately or independently in different scientific disciplines and practiced in different industrial sectors (Fig. 5). To promote in-depth fundamental research and theoretical breakthroughs in thermochemical reactions, ETC aims to develop and utilize a particular set of theories and methods for structuring knowledge and experience in the field.

Essentially, ETC investigates characteristic thermochemical reactions and their interacting reaction network for scientific fundamentals (e.g., chemistry and physics) and engineering techniques concerning a specific reaction or reaction process. With the target of engineering a reaction, the investigation has to be at different scales covering micro (or particles), reactor, and process. Special emphasis should be placed on optimizing the interactive matching between heating and reactions, as illustrated in Fig. 6. At the microscale, the investigation is generally

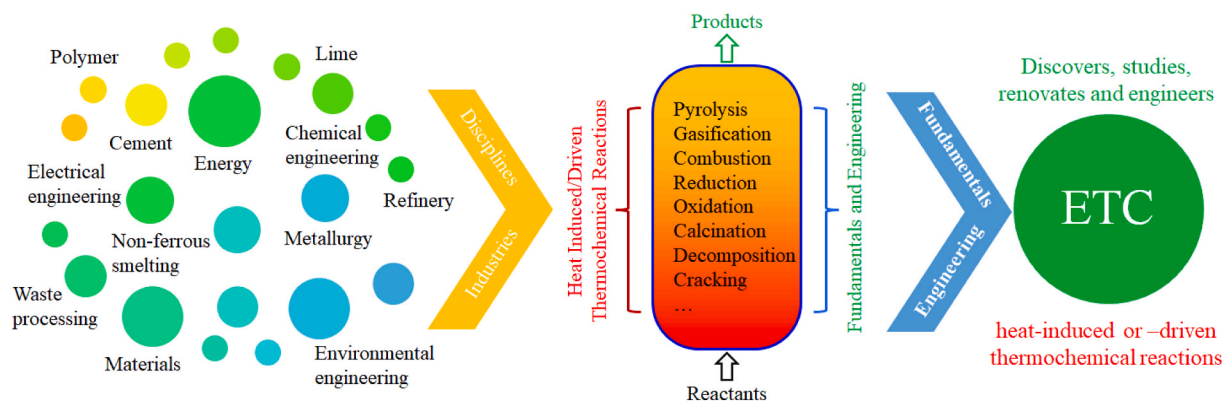


Fig. 4. Engineering thermochemistry collaborates with fellow disciplines and industries.

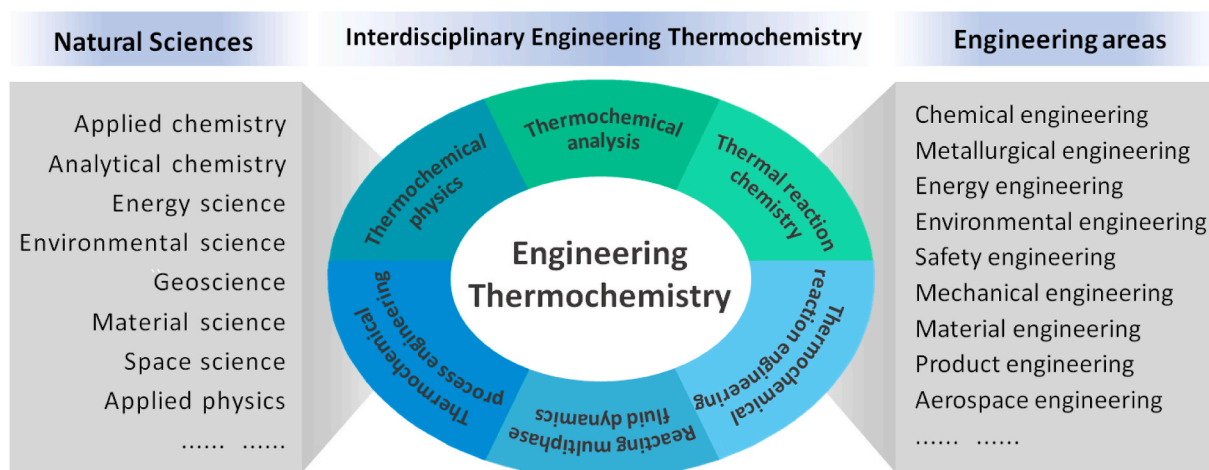


Fig. 5. Disciplinary concept of engineering thermochemistry.

ETC: Interactive matching between heating and reaction at multiple scales

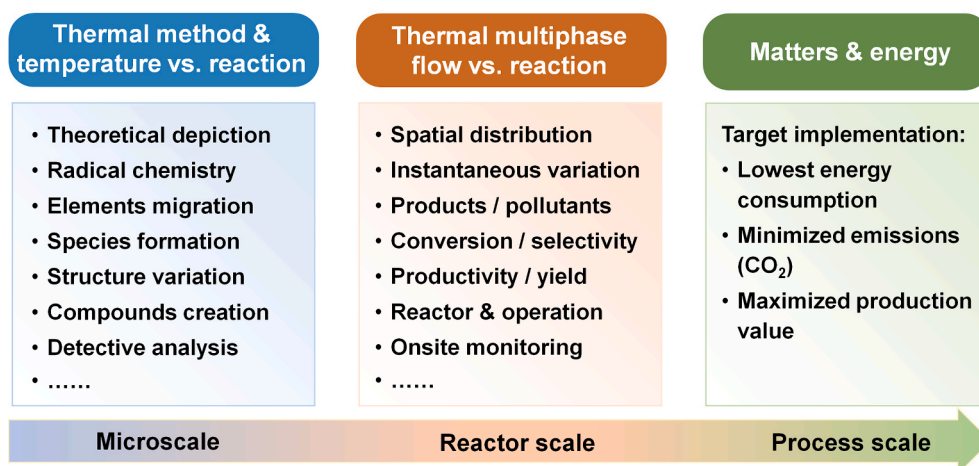


Fig. 6. Mechanism of engineering thermochemistry approach for innovation.

made to understand qualitatively or quantitatively how heating method and temperature impact the thermochemical reactions in terms of, for example, radical (fragment) chemistry, elements migration, species formation, structure variation, compounds creation, and so on. Meanwhile, theoretical depiction and detective analysis of characteristic thermochemical reactions are highly demanded for reaction characterization at this scale. Inside a reactor, the conditions of a specific reaction are subject to multiphase flowing dynamics and mass/heat transfer behavior. As such, obtaining the interrelationships between multiphase fluidynamics/transfer and reaction performances is of critical importance for implementing engineering development of the investigated reaction or reaction system. For this scale, the crucial characteristics or factors deserving to be investigated would include spatial distribution, instantaneous variation, products and pollutants, conversion and product selectivity, productivity and yield, reactor operation, and onsite monitoring. Up to the scale of process, the focus is to optimize the overall conversion and utilization of both matters and energy, and meanwhile to maximize the economics as well. With regard to a specific innovation or development, the consequence is usually a compromise of the prime targets including the possibly lowest energy consumption, minimized emissions (particularly CO_2), and maximized production value.

On the basis of the fundamental knowledge about reactions and their engineering, ETC explores every avenue towards the creation of the

most suitable environment and conditions (e.g., reactor configuration, temperature, residence time, flow pattern, and mixing) for implementing thermochemical reactions to meet their process and product requirements. Ultimately, ETC identifies and resolves issues of reaction engineering and process engineering in order to successfully transform raw materials into targeted products industrially via investigated thermochemical reactions. Following the ETC principles and approaches, we are empowered to develop green, energy-efficient, and environmentally friendly resource and material conversion processes, equipment, and analytical tools. As such, we believe that ETC can play a vital and irreplaceable role in transforming the energy-intensive CO_2 super-emitting processes into advanced ones with low energy consumption, low carbon emission, and low waste generation.

3. Characteristics of energy-intensive processes

As presented previously, the CO_2 super-emitters fall into three categories: coal-fired combustion processes, electrolytic and electric heating processes, and high-temperature thermal processes charged with chunk feedstocks. In the following sections, we briefly present the characteristics of these processes (Table 1).

Table 1
Characteristics of energy-intensive processes in China.

Energy-intensive processes in China	Applications	Typical reactors	Primary energy efficiency	Annual energy consumption	Annual CO ₂ emission
Coal-fired processes	Power generation	Fluidized beds	~40%	2111 million tons of standard coal ^a	5.62 billion tons ^a
	Industrial heat supply	Grate furnaces, fluidized beds	60–65%	1142 million tons of standard coal ^a	3.03 billion tons ^a
Electrolytic and electric-heating processes	Production of aluminum, copper, nickel, etc.	Electrolytic reactors	~20%	~500 TWh of electricity ^{a, b}	~400 million tons ^d
	Production of ferrosilicon, metallurgical silicon, calcium carbide, etc.	Electric-arc furnaces	~20%	~250 TWh of electricity ^{a, b}	~200 million tons ^d
High-temperature thermochemical processes	Production of pig iron, cement clinker, lime, glass, etc.	Shaft or rotary kilns	<50%	~750 million tons of standard coal ^{a, c}	~2000 million tons ^{a, c}

^a Calculated by data from (CEADs, 2022a, b; NBS, 2022).

^b Calculated by data from personal communications.

^c Calculated by data from (Shan et al., 2016, 2019).

^d Calculated at current coal-combustion-dominated electric power efficiency (i.e., ~40%) (CEC, 2022).

3.1. Coal-fired processes

Coal-fired power generation is the largest coal consumer in some countries. In 2020, China consumed 2111 million tons of standard coal for power and steam generation, accounting for 52% of national total coal consumption. Among coal-fired power plants, about one-third of plants operate in subcritical conditions with an average power supply efficiency of only about 30%, while reset plants operate in supercritical and ultra-supercritical generators with a power supply efficiency of 38%–50% (Wang et al., 2021). Currently, the national average power supply efficiency is approximately 40% (CEC, 2022).

Next to utilities, China's manufacturing industries (such as food, textile, paper, chemical, petrochemical, materials, machinery, and waste processing) are the second largest user of coal-fired industrial boilers, consuming approximately 28% or 1142 million tons of standard coal annually. Industrial boilers are predominately grate-fired and broadly distributed geographically, and most of these boilers have relatively low capacity and efficiency. Overall, the energy efficiency of industrial boilers is 60–65%, about 10–15% lower than the international advanced performance level (Yue et al., 2018; Zhang et al., 2018).

In addition, district heating systems and various small coal stoves are

prevalent in the colder areas of northern China, consuming over 100 million tons of standard coal by nearly 100 million households and commercial consumers (Liu et al., 2019). Most of these small-to-medium-sized boilers and stoves are highly inefficient, with energy efficiencies lower than 50% (Liang et al., 2017).

3.2. Electrolytic and electric-heating processes

In many industries, typically ferrous and non-ferrous metallurgy, chemical, and material, electricity is used to heat reactors to produce specific products. Electrolytic reactors and electric-arc furnaces are the two main types of reactors used in these processes (Fig. 7). Due to various practical issues, the thermal efficiency of electrolytic and electrical heating systems is usually less than 50%, corresponding to a primary energy efficiency of less than 20% at current coal-combustion-dominated electric power efficiency (i.e., ~40%).

Electrolytic reactors are the primary devices for producing aluminum, copper, nickel, and many other metallic powder materials through electrochemical reactions with the help of electric current in an electrolyte solution. The electrolytic process is usually energy-consuming (Fig. 8). For instance, electrolytic aluminum productions

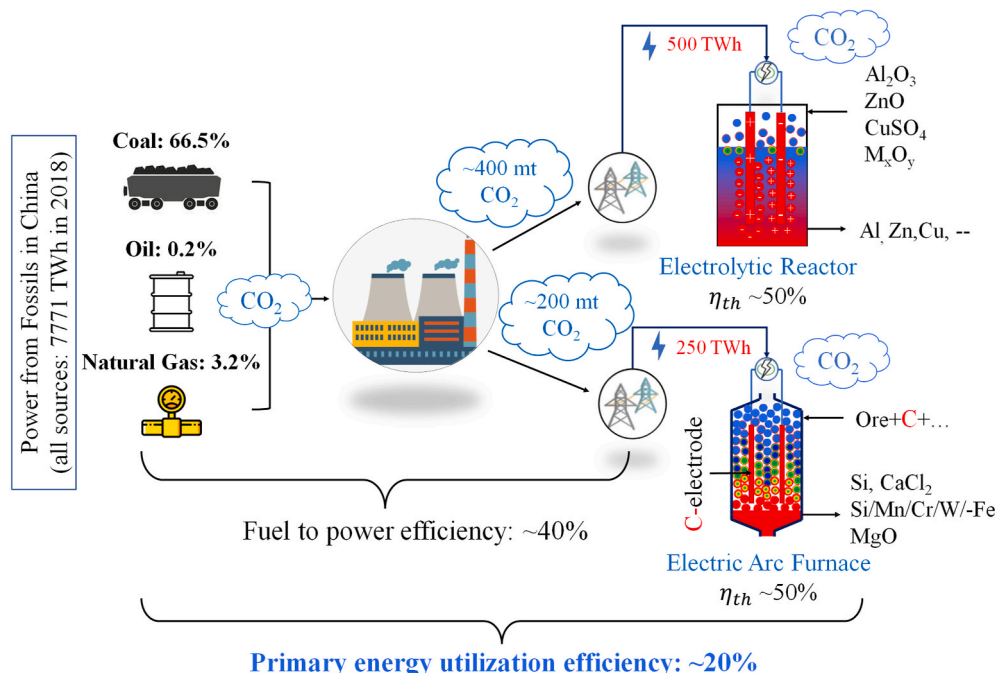


Fig. 7. Electrolytic and electro-thermal processes.

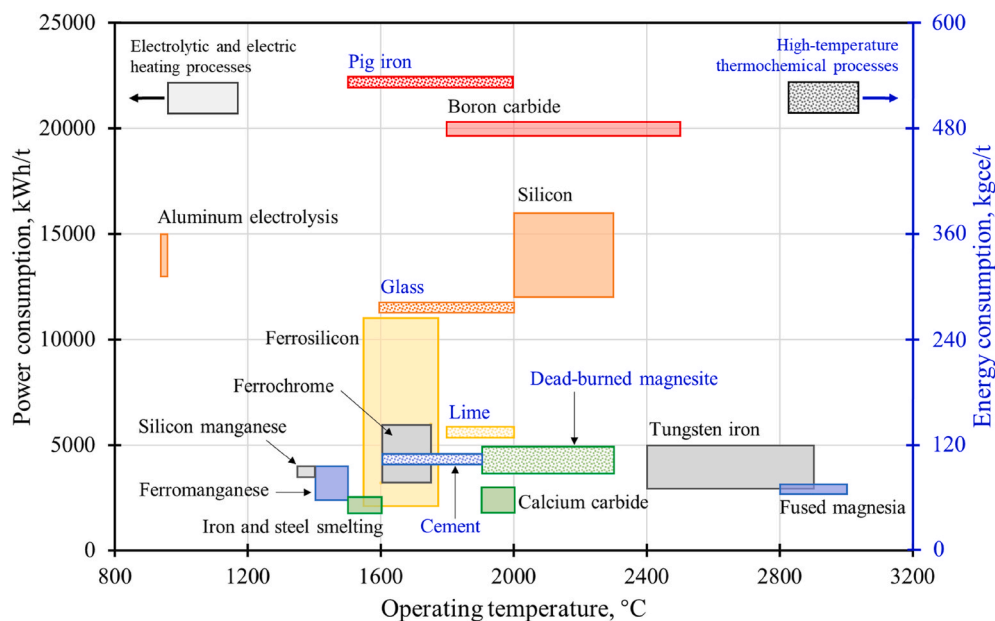


Fig. 8. Energy consumption of typical electrolytic and electric heating processes and high-temperature thermochemical processes in China.

consume some 13000–15000 kWh per ton-Al. The process alone consumes a total of about 6.4 percent of electricity generated nationally in China (Wang and Xu, 2022). As a result, the process emits an estimated 400 million tons of carbon dioxide, equivalent to about 4% of the country's total emissions.

Electrical heating processes usually use electric-arc furnaces. Today, electric-arc furnaces are widely used to process mineral materials and produce metallurgical and chemical products, e.g., ferrosilicon, ferromanganese, ferrochrome, iron tungsten, silicon manganese alloy, metallurgical silicon, and calcium carbide (Fig. 8). These processes are characterized by high operating temperature (i.e., 1300–3000 °C) and high electric power consumption (3000–20000 kWh per ton product). Altogether, we estimate that the electrical heating furnaces consume about 250 TWh of electricity, or 3.2% of China's annual electrical power consumption, resulting in nearly 200 million tons or about 2% of the national total CO₂ emissions from energy use only.

3.3. High-temperature thermochemical processes

Direct fuel combustion provides the required heat energy in some

thermochemical conversion processes. The typical processes include the production of pig iron, cement clinker, lime, glass, ceramics, refractory materials (e.g., dead-burned magnesia), and many others (Fig. 8). These processes operate at high temperatures (i.e., 1500–2300 °C), and reaction time usually ranges from minutes to hours or even days. As such, these processes are energy-consuming and carbon-emission intensive.

In these processes, shaft or rotary kilns (called blast furnaces in the case of pig iron production) are generally used to transform raw materials into products (Fig. 9). Raw materials must be large-sized, typically from 5 to 150 mm, to ensure the permeability of gas flows in these reactors since small particles can be packed tightly, causing blockage or other operational issues. Using large-sized materials inherently lowers heat transfer rates between the gas stream and solid materials, leading to long process times and low capacities. The low gas-solid heat transfer rate makes it hard to recover heat effectively from high-temperature products. Thus, the thermal energy efficiency of these processes is generally below 50%.

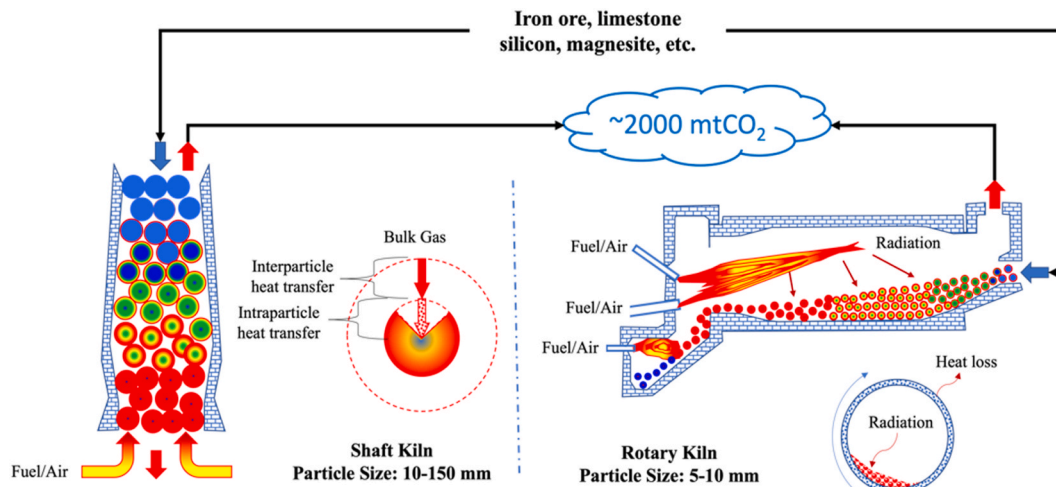


Fig. 9. Schematics of the high-temperature shaft and rotary kilns.

4. ETC routes to reduce CO₂ emissions

Focusing on the aforementioned super-emission thermochemical processes, we have conducted a thorough analysis and careful examination of alternative technologies that have the potential to reduce CO₂ emissions effectively and quickly. From the perspective of ETC, we identified three pathways toward carbon neutrality (Xu et al., 2022): carbon emission reduction, carbon substitution, and carbon recycling. Fig. 10 briefly summarizes the major ETC technical solutions corresponding to these three pathways to reduce CO₂ emissions from the specific super-emitting processes. In the following sections, we elaborate further on these ETC technical solutions.

4.1. Carbon emissions reduction

Carbon emission reduction at source is the most direct and effective pathway toward carbon neutrality, a technical solution that reduces carbon emissions while continuing to sustain and promote social and economic development. The first on the list of priorities is reducing CO₂ emissions from coal combustion processes. The fundamental strategy relies upon increasing energy efficiency by effective use of high-quality energy and reduction in heat losses. Fig. 11 shows that under specified conditions, approximately 2.3 billion tons of CO₂ emissions can be reduced annually in China based on the country's coal consumption data in 2020.

Next, unprecedented efforts need to be made to innovate electrically powered or heated thermochemical reactions, which are exceedingly low in primary energy utilization. One approach is, of course, replacing fossils-dominated electricity with “green” electricity when it is possible. Another approach, perhaps the most important and effective, is to change the processes to use heat from burning fuels (fossils or renewables) instead of heating by electricity. Assuming that electrical power can be replaced with thermal energy in these processes, the primary energy utilization efficiency will be increased from today's below 20%–80% plus, resulting in ~650 million tons of CO₂ emission reductions

based on the estimated power consumption data in 2020.

Lastly, close attention needs to be given to increasing the energy efficiency of high-temperature thermochemical processes that manufacture cement clinker, lime, pig iron, and many others. From the view of ETC, the most effective approach here is to innovate reactor technologies and make it possible to process feedstocks of small particles. Processing small particles can effectively lower reaction temperature and time because of significantly enhanced heat and mass transfer, thereby considerably saving energy consumption and CO₂ emissions. We estimate that over 800 million tons of CO₂ emissions can be reduced from these high-temperature thermochemical processes if their energy efficiency increases to 85%.

Overall, successful implementations of ETC approaches can reduce approximately 3 billion tons of CO₂ emissions from the targeted CO₂ super-emitters in China. In the following sections, we will provide more detailed information about these analyses while highlighting the vital roles of ETC in achieving these objectives.

4.1.1. Increasing efficiency of electric power generation

Current coal-fired power generation is theoretically limited by the Carnot cycle efficiency, in addition to problems associated with low steam parameters, high energy loss in condensing and recycling steam water, and ineffective use of high-quality coal constituents (i.e., volatiles). Accordingly, we propose the following three ETC approaches to resolve these problems.

1) Ultra-supercritical power generation.

As mentioned previously, the average power generation efficiency of China's fossil fuel power plants is about 40% because many small- and medium-sized power generators operate in subcritical conditions. To improve power generation efficiency, it is a high priority to retrofit these inefficient generators with efficient supercritical or ultra-supercritical units. Currently, most ultra-supercritical generators operate at a steam temperature of 600 °C and a pressure of about 28 MPa. Advanced ultra-

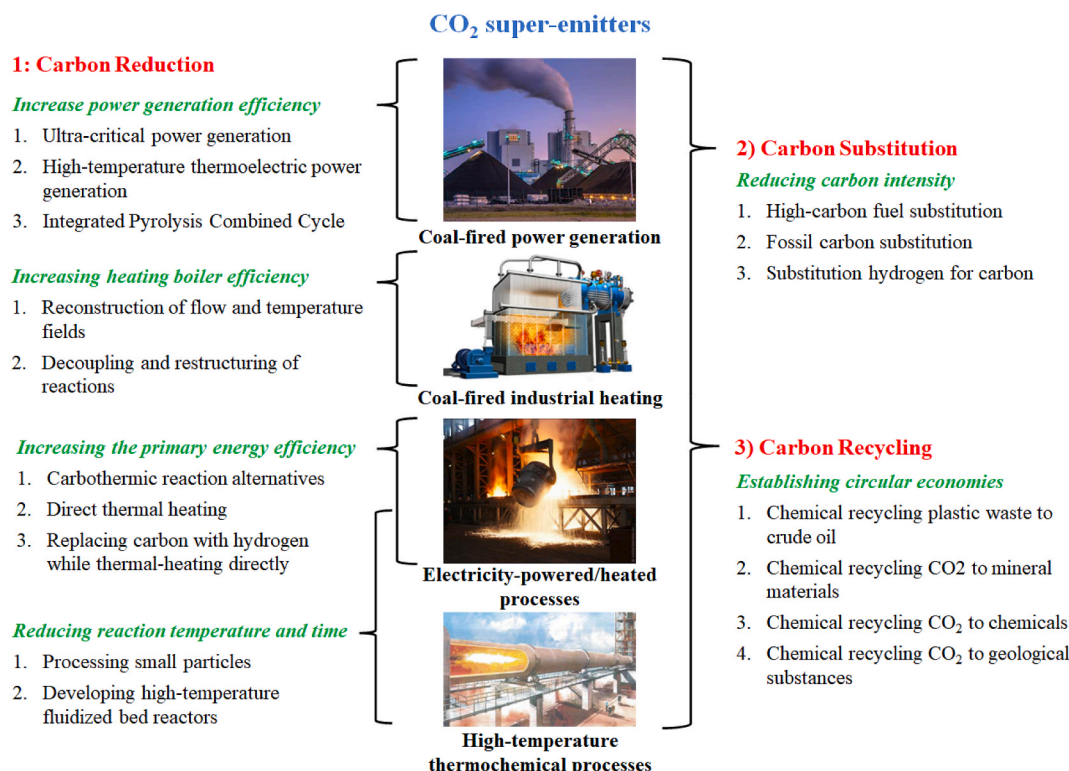


Fig. 10. Effective ETC approaches to reduce CO₂ emissions from super-emission processes.

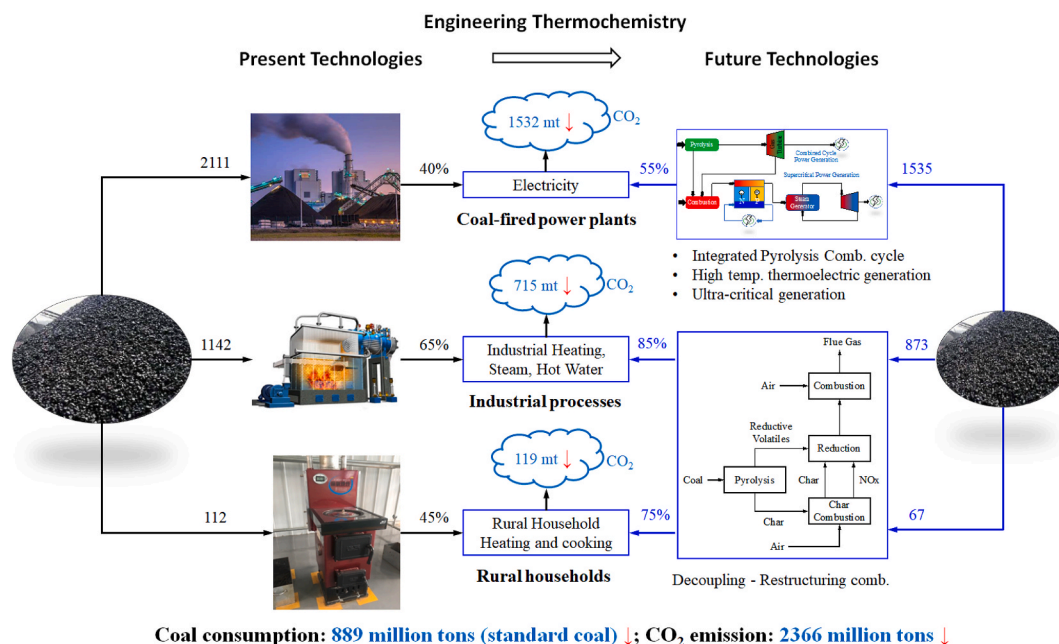


Fig. 11. Increasing efficiency of coal-fired processes to reduce CO₂ emissions significantly based on China's coal consumption data in 2020.

supercritical power generators operating at steam temperatures exceeding 700 °C are under active development. Combined with technical measures such as secondary reheating, flue gas waste-heat recovery, back pressure reduction, patristic power saving, and feed water temperature increase, the advanced ultra-supercritical power generation plants can increase the power generation efficiency to ~50% (Wang et al., 2021).

2) High-temperature thermoelectric power generation

It is worth noting that even under ultra-supercritical conditions, the maximum steam (water side) temperature today is 720 °C, which is lower than the flue gas (fireside) temperature above 1400 °C in combustion furnaces. This means that the current Carnot-cycle-based power generation technology (i.e., steam turbine) does not fully and efficiently use the high-grade (i.e., high temperature) thermal energy from combustion. One technology to utilize high-temperature energy effectively is the thermoelectric power generation (TEG) using a phenomenon known as “the Seebeck Effect” that describes the direct conversion of thermal energy to electricity based on a temperature differential between the two sides of a thermoelectric module. By now, there are numerous practical applications of TEG implemented at temperatures less than 180 °C, ranging from employing green resources to exploitation of industrial waste heat (Faddouli et al., 2023; Khanmohammadi et al., 2020; Pourkiaei et al., 2019). For high-temperature TEG (>650 °C), however, it is still in an early stage of development due to the lack of high-performance materials and mature thermoelectric devices. Efforts should be made to move this field to the next level that is closer to commercialization. Currently, the available thermoelectric semiconductor materials can achieve power generation efficiencies of 6–11% at hot side temperatures high as 800 °C (Tan et al., 2019; Wang et al., 2013). Going forward, we encourage researchers to put more effort into development of novel thermoelectric materials working efficiently and stably at temperatures above 1000 °C as well as engineering novel thermoelectric devices employing such materials. Here, thermochemical physics investigating physical changes in materials/reactants with temperature or during thermochemical reactions, a main scope of ETC (see Fig. 5), can significantly guide the innovation on high-temperature material synthesis strategies and development of high-temperature thermoelectric materials for their desired performance and stability as

well as their large-scale production.

3) Integrated pyrolysis combined cycle

Coal is a complex substance of hydrocarbons and can be considered to be composed of hydrogen-rich volatiles and carbon-rich char as main constituents. These constituents are combusted simultaneously in today's coal-fired boilers. In this way, it does not leverage the qualities and values of hydrogen-rich volatiles in terms of high energy content, ease of combustion, and usefulness for NO_x control. To make the best use of coal constituents based on their quality, we recommend an advanced power and heating generation system called an integrated pyrolysis combined cycle (IPCC) system. Unlike the IPCC system that Eric et al. (Sandvig et al., 2003) presented, in which the liquid oil is produced to serve as fuel for a gas turbine topping cycle, the advanced IPCC proposed herein does not produce liquid oil but only a hydrogen-rich gaseous fuel and a carbon-rich char. Compared with its cousin technology IGCC (integrated gasification combined cycle), IPCC requires a low level of integration and thus low capital investment. Without liquid oil production, the advanced IPCC overcomes the technical and operational obstacles caused by it, such as dust contamination, clogging and corrosion of pipelines and equipment. Determined by these advantages, the advanced IPCC is more adaptable for commercial power generation with competitive efficiency and economics.

In the advanced IPCC system, the gaseous fuel, known as pyrolysis gas, is sent to a gas turbine topping cycle to generate power, with an efficiency of potentially up to 65% (Mom, 2013). The exhaust heat from the gas turbine, together with the combustion of char, provides the thermal energy for an ultra-supercritical steam turbine as the bottoming cycle to generate more power. Into this combined cycle the thermoelectric transformation is further integrated. Thus, the total load of steam cycle is actually much reduced to considerably decrease the latent heat loss caused in condensing and recycling the low-pressure steam downstream the steam turbine.

Fig. 12 presents a conceptual illustration of such a power generation system integrating the three key technologies. Overall, this IPCC makes the best use of coal constituents based on their qualities and high-temperature thermal energy. It has the potential to convert coal to electricity with an efficiency of 55–65% (Mom, 2013). The overall energy efficiency of the advanced IPCC can be further increased by 20% if

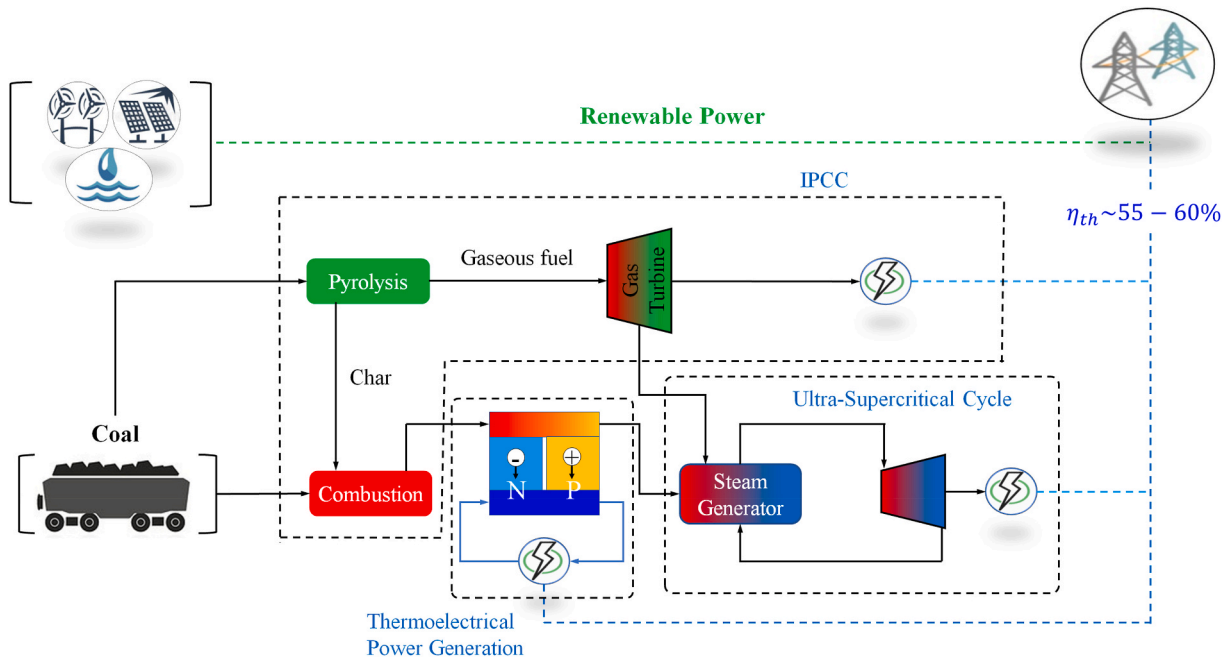


Fig. 12. A schematic of a highly efficient electric power generation system.

it is integrated with combined heat and power (CHP) production (Karvonen et al., 2018), providing an excellent way to retrofit a vast number of small-scale CHP power plants. Once this efficiency target is achieved, China's power generation sector alone could reduce carbon dioxide emissions by 1.5 billion tons (see Fig. 11) while still outputting as much power as it does today to meet the consumption demand.

The new power generation technologies described above are promising but entail some technical challenges. The essence of challenges is in relation to high-temperature materials, such as functional materials for efficient thermoelectric power generation at hot side temperatures above 1000 °C and metallic alloys withstanding over 700 °C for ultra-supercritical combined cycles. The manufacture of these materials involves multiple scientific disciplines and process industries, such as thermochemistry, thermochemical physics, engineering material, metallurgy, and chemical engineering. For this reason, by its interdisciplinary nature (Fig. 5), we expect that ETC will play a significantly

decisive role in the design, development, and production of advanced high-temperature materials.

4.1.2. Increasing efficiency of industrial heating boilers

Currently, industrial heating is served mainly by coal-fired grate furnaces and a small number of circulating fluidized bed boilers. These boilers are designed with conventional combustion technology and characterized by inadequate flow and temperature fields (Fig. 13(a)). Consequently, boiler efficiency is low due to incomplete combustion, and NO_x emission is high as a result of high temperature and improper distribution of oxygen. To innovate industrial heating boilers, we address the two ETC approaches: decoupling and restructuring of reactions and restructuring of flow and temperature fields.

1) Decoupling and restructuring of reactions

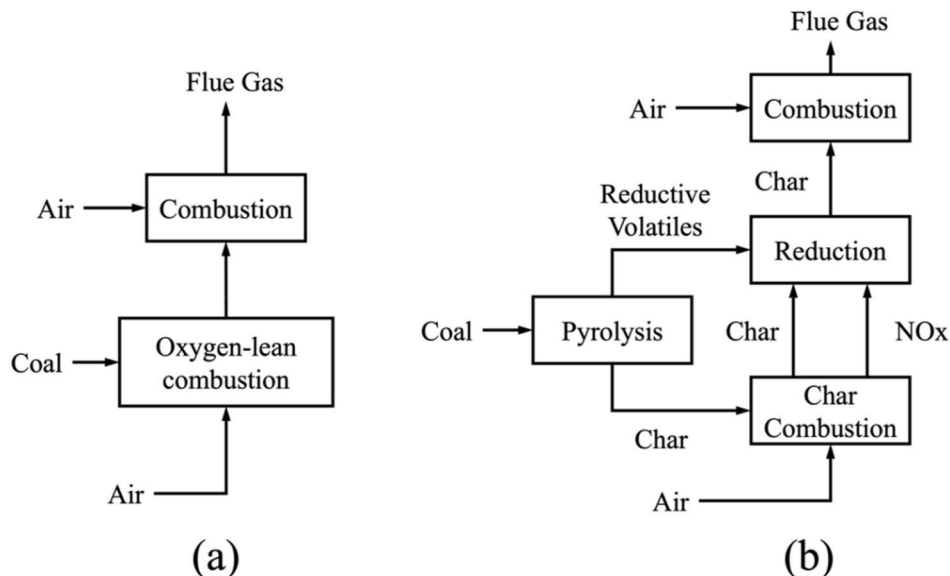


Fig. 13. Schematic illustrations of principles for (a) conventional combustion and (b) decoupling and restructuring combustion (Han et al., 2018).

In theory, the global combustion reaction can be decoupled into individual characteristic reactions (e.g., pyrolysis, gasification, combustion). These individual reactions, if possible, can be reorganized to occur temporally and/or spatially in a preferable sequence or interaction pattern. In this case, the multiphase flow field, air/oxygen supply, and temperature distribution can be structured to provide the best possible environment for each and all reactions; thus, the best possible combustion performance and emission control can be obtained. This technique is called decoupling and restructuring of reactions (DRR) (Han et al., 2018; Zhang et al., 2013), as schematically illustrated for solid fuel (coal) combustion in Fig. 13(b).

DRR is one of the major approaches of ETC and is particularly useful for innovating thermochemical reactions. Based on the DRR principle, an advanced chain grate-fired furnace has been designed, as schematically illustrated in Fig. 14(a). The new furnace has a pre-combustion and pyrolysis section at its entrance. In this section, coal is first pyrolyzed in the absence or insufficiency of oxygen to produce hydrogen-rich volatile fuel gases and carbon-rich char. The pyrolysis conditions (i.e., temperature and time) are controlled to yield the best product profiles (e.g., yields of light gases and high-molecule oil) and physicochemical structures of generated char particles (e.g., pore size, pore volume, and the degree of pyrolysis). The hydrogen-rich and hence reductive volatile fuel gases flow to and mix with flue gas from char combustion downstream in the furnace top space, where the harmful NO_x produced from char combustion is reduced to harmless N₂. At the char combustion zone, complete combustion of char with low NO_x emissions is achieved by controlling air supply and combustion temperature. Experimental studies have demonstrated that the new design can increase the thermal efficiency of the chain furnace from generally below 65% up to 85% and reduce the NO emission by no less than 50% (Liu et al., 2022).

Fig. 14(b) shows an advanced grate-fired stove designed based on the DRR method (Li et al., 1995; Liang et al., 2019, 2022). The stove is structured to have a pyrolysis zone, a char combustion zone, and a burning-out zone. Solid fuel in the pyrolysis zone is heated by the heat transferred from the adjacent combustion zone, and part of the fuel-N evolves as nitrogen N₂ in the pyrolysis. On the top of an inclined grate, char particles are combusted with air introduced through the grate. The flue gas enters the after-combustion chamber, where char fines and fuel gases burn out with secondary air. In practical operations, ETC requires that the combustion field (i.e., atmosphere, temperature, etc.) above the grate be optimized to ensure low NO_x emission and effective combustion of combustible gases and semicoke (He et al., 2006). Experimental studies have demonstrated that the combustion efficiency and thermal efficiency of this decoupling stove can reach more than 98% and 75% (Liang et al., 2017), respectively. At this thermal efficiency, Chinese households' coal-fired stoves can save 45 million tons of standard coal and cut about 120 million tons of CO₂

emissions annually.

2) Reconstruction of flow and temperature fields

In the view of ETC, the performance of a thermochemical reaction is greatly affected by the multiphase flow and temperature distribution fields. This fact can be explicitly explained by the designs of coal-fired circulating fluidized bed (CFB) boilers. Traditional CFB boilers are generally characterized by a bubbling bed of coarse particles (with sizes up to 10 mm) at the bottom and a dilute region at the top formed by entrained fine particles (Fig. 15(a)). Coal particles are almost completely combusted in the bottom dense fluidized bed at high temperatures and oxygen-rich conditions, the conditions that are not conducive to low NO_x control. Due to the limited entrainment of fine particles, the solids concentration at the top region is low, which leads to a low heat transfer rate between the bed and water-wall membranes and, thereby, low thermal load capacity.

To overcome the shortcomings of conventional CFB boilers, an advanced CFB boiler has been designed via principles of reaction decoupling (Han et al., 2016; Yao et al., 2011; Zhang et al., 2013), as schematically illustrated in Fig. 15(b). A dual fluidized bed system is configured to accomplish combustion reaction decoupling and restructuring: coal pyrolysis in a fluidized bed pyrolyzer installed underneath the cyclone separator, combustion of char in the bottom region of the riser reactor, and reactions between volatiles, char, and NO_x at the upper region of the riser reactor. The gas-solids flow patterns at the bed bottom and top regions are restructured to enhance these reactions. Specifically, the new CFB design follows the approach known as fluidization state specification (Li et al., 2016; Yue et al., 2017). The core of this approach is increasing the solids circulation rate so that the fluidization patterns at the bottom and top regions can be set at the states that favor efficient combustion, NO_x reduction, and heat transfer between the bed and water-membrane walls.

The advanced CFB technology described above has been successfully commissioned commercially for efficient and low-NO_x combustion of coal and biomass fuels (Han et al., 2018). So, we encourage industrial heating consumers to consider advanced CFB technology because it can achieve a thermal efficiency of over 90% with NO_x emission in compliance with the stringent emission standards without flue gas treatment required. As the CO₂ emissions are concerned, it is estimated that over 700 million tons of CO₂ emissions can be avoided in China annually if the thermal efficiency of industrial boilers increases to 85% (see Fig. 11).

4.1.3. Increase efficiency of electricity-consuming thermochemical processes

Currently, there are two thermochemical approaches to improve the

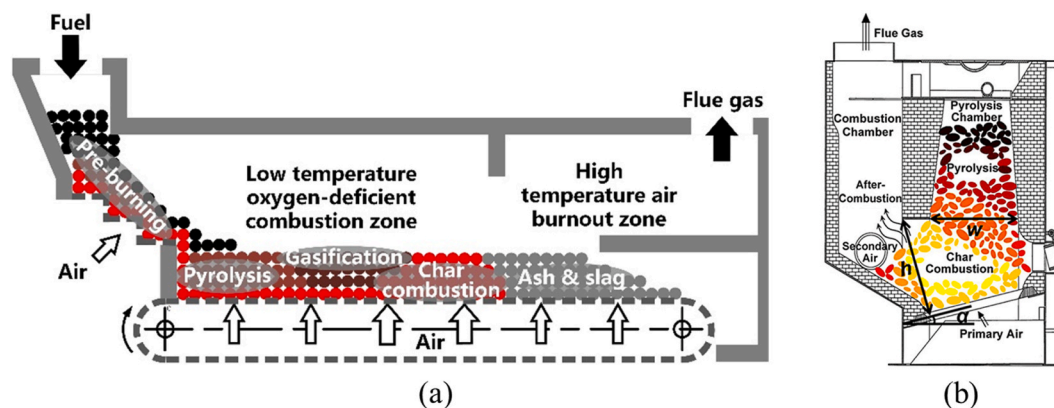


Fig. 14. Schematic illustrations of (a) an advanced chain furnace designed and (b) a grate-fired stove based on decoupling and restructuring combustion (Liu et al., 2022).

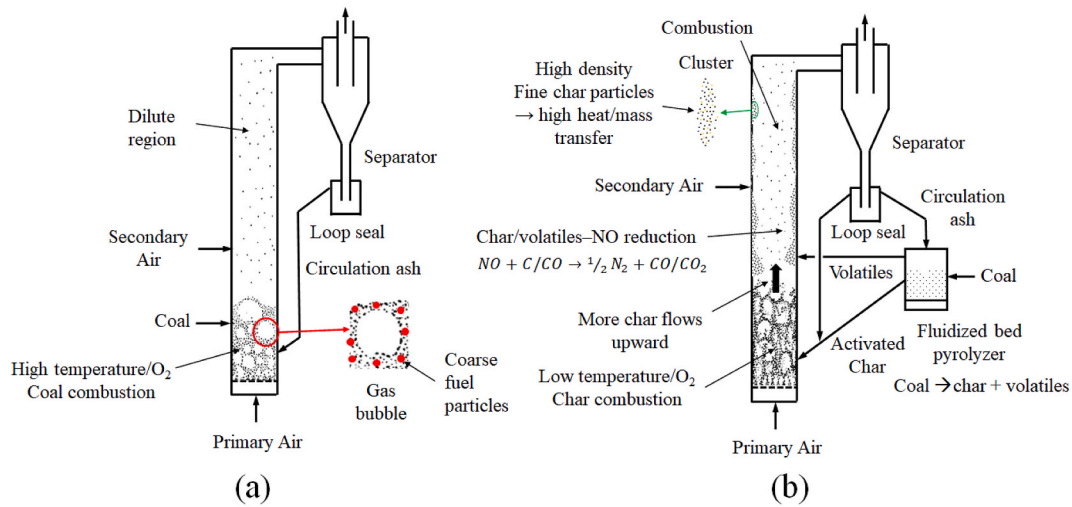


Fig. 15. Schematic illustrations of (a) a conventional CFB and (b) a CFB based on decoupling and restructuring of reactions (Han et al., 2018; Liu et al., 2022).

primary energy utilization efficiency of these processes: 1) using non-electrolytic carbothermic alternatives and 2) using thermal energy to replace electricity. We illustrate the effectiveness of these ETC approaches further in the following sections with several examples.

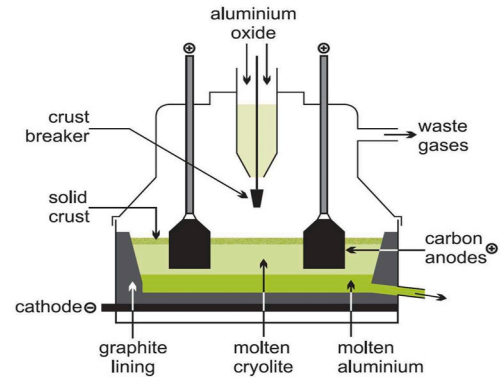
1) Alternative carbothermic reactions

Carbothermic reduction reactions are a type of chemical reaction in which the reduction of substances such as metal oxides occurs in the presence of carbon as the reducing agent and therefore are very useful in the production of the elemental forms of many elements. One example is the production of primary aluminum.

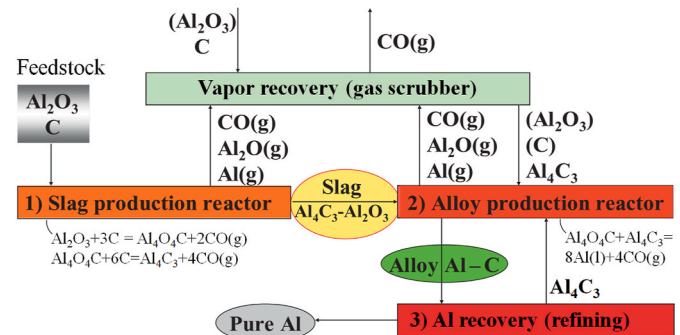
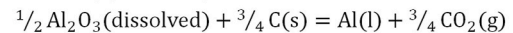
It is well known that the primary aluminum has been industrially produced by two energy-intensive processes, the Bayer process and Hall-Héroult process, which were developed in the late 1800s. The Hall-Héroult process uses an electrolytic reactor to produce primary aluminum from the relatively high-purity alumina prepared by the Bayer process from bauxite. In the electrolytic process, aluminum oxide (or alumina, Al₂O₃) is dissolved in an electrolyte consisting mainly of molten cryolite (Na₃AlF₆) and aluminum fluoride (AlF₃) at 950–970 °C. Aluminum precipitates in liquid form at the carbon cathode, and oxygen escapes as carbon dioxide gas at the carbon anode. The aluminum electrolysis consumes about 13,000 to 15,000 kWh of power for every ton of primary aluminum. Additionally, aluminum smelters use carbon anodes in their electrolysis cells because carbon is a reasonably good electrical conductor and can withstand the corrosive electrolyte containing fluoride at about 960 °C. As shown in Fig. 16(a), the carbon anodes are also an active reactant of the electrochemical reaction, contributing to additional CO₂ emissions.

For many years, efforts have been made to find alternative smelting technologies to replace the centuries-old energy-intensive Hall-Héroult process (Cochran, 2016; Kvande and Drablos, 2014). Among the potential alternatives, the carbothermic reduction of alumina is promising, although the idea is also an old dream (Kvande and Drablos, 2014). Compared with the electrolytic process, the carbothermic process uses carbon and heat to reduce alumina to aluminum (Fig. 16(b)). The reaction proceeds at ~2000 °C without electrolysis involved. The process can reduce energy consumption by more than 30% over the Hall-Héroult process (Bruno, 2003), although the electric current is still used to heat alumina and carbon. This energy saving will cut electricity consumption by about 150 TWh a year in China, with a corresponding CO₂ emission reduction of 120 million tons. Because of technical issues such as controlling side reactions and removing impurities from the products, the carbothermic process has not yet been commercialized.

Given the massive potential of carbon emission reduction, it is well



(a) Electrolytic overall reaction:



(b) Carbothermic overall reaction:

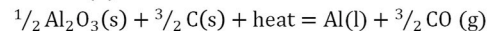


Fig. 16. (a) A conventional electrolytic process, and (b) an alternative carbothermic process for aluminum production (Bruno, 2003; Kvande and Drablos, 2014).

worth continuing to research and develop alternative aluminum production technologies, particularly carbothermic processes that use thermal energy to replace electric heating.

2) Direct thermal heating

For high-temperature endothermic reactions, the direct combustion

of a fuel or the use of solar thermal energy (Guene Lougou et al., 2020; Wu et al., 2023) to provide the heat required for the reaction is shown to be the most effective method of energy utilization. Therefore, replacing electricity used for heating reaction processes with thermal energy is attractive in improving energy efficiency. The development of an oxygen-thermal method as an alternative to the traditional electric-arc furnace in the production of calcium carbide (CaC_2) is a perfect example of such efforts.

Calcium carbide (CaC_2) is known as an important chemical material used to produce a variety of valuable chemicals, such as acetylene and acetylene-derived products (e.g., polyethylene, polyvinyl chloride, vinyl acetic acid, and 1,4-butyl glycol, fertilizers, steelmaking). It is produced by a mixture of CaO and coke (carbon) in an electric-arc furnace at about 2000°C (Fig. 17(a)). The method of calcium carbide production has not changed since its invention in 1888. As the world's largest calcium carbide producer, China has recently produced over 28 million tons of calcium carbide a year, consuming more than 92 GWh of electricity. Because electricity is generated mainly from fossil fuels in China, the primary energy utilization is extremely low for the production of CaC_2 .

Over the years, a lot of efforts have been put into seeking alternative technologies that are energy-efficient, environmentally friendly, and low-cost (Wang et al., 2014; Xu et al., 2021). Among the tested technologies, the autothermal oxygen-thermal process deserves attention (Fig. 17(b)) (Mi et al., 2014). In this process, the reaction heat required to synthesize CaC_2 is provided by burning part of carbon-containing raw materials with oxygen-rich gas in the reactor. As shown in Fig. 17(c), the oxygen-thermal method can save 80% of energy and reduce 56% of CO_2 emissions compared with the electro-thermal methods for CaC_2 production. Despite these advantages, the thermal heating method has two significant issues that remain to be resolved. First, the process consumes more coke than the electric-arc heating process and thus produces a large amount of CO , which must be recovered and used in other processes (Wang et al., 2014). Second, the increased consumption of coke increases the contamination of the products because coke contains ash, thereby lowering the product quality. Because of these issues, the oxygen-thermal method has not yet been industrialized; thus, the future calls for more fundamental research and technological innovation to bring the technology to successful industrial operations.

Clearly, replacing electricity with thermal energy can effectively improve the energy efficiency in these conventional electric-arc furnace processes. Assuming all major electric-arc furnace processes (Fig. 8) are converted to thermal heating, we estimate ~ 200 million tons of CO_2 emissions can be reduced annually in China.

3) Replacing carbon with hydrogen while thermal-heating directly

Most of the electrical heating processes (see Fig. 8) involve carbo-thermic reduction reactions, involving the reduction of substances using carbon as the reducing agent. Hence, for these reactions, CO_2 emissions come from two sources: process heating (i.e., energy-related) and carbon conversion (i.e., process-related).

For instance, as an important raw material in the production of steel, cast irons, alloys, ceramics, silicon-based polymers, photovoltaic cells, electronics, semiconductors, and among many others, metallurgical grade silicon (MG-Si) has been produced in submerged electric-arc furnaces by reducing high-quality quartz with carbon-rich materials (charcoal, coke, etc.) (Maurits, 2014; Kakalashe and Tangstad, 2011). To reduce CO_2 emissions from MG-Si production, we strongly recommend developing alternative technologies that use not only thermal energy to replace electricity but also renewable carbon or hydrogen as the reducing agent (Zhou et al., 2021). Using “green” hydrogen as a reducing agent ($\text{SiO}_2 + 2\text{H}_2 \rightarrow \text{Si} + 2\text{H}_2\text{O}$) not only avoids the process CO_2 emissions but also significantly reduces the reaction temperature, especially when small-sized particles are processed in reactors. An additional benefit of the hydrogen-thermal reduction method is that it does not produce intermediate SiC , so the yield of silicon is high. The technique can make high-purity solar-grade silicon directly without purification required, and we are convinced that it is a future technology worth continuous research and development.

4.1.4. Reducing reaction temperature and time

The thermochemical reaction processes shown in Fig. 8 operate at temperatures around 2000°C in electric-arc furnaces, shaft kilns, or rotary kilns, although most of them can theoretically occur at significantly low temperatures. Chunk feeds (generally 5–150 mm in size) are typically required in these reactors because they facilitate stable and safe operations by providing them with better gas permeability and lower pressure drop. However, processing large-size materials hinder heat transfer and contact efficiency. For example, when the particle diameter is increased from 1 mm to 30 mm, the time required to heat the particle center to 1600°C is increased by approximately 10000 times in a gas stream of 2000°C (Fig. 18(a)), and the contact point between particles is reduced by 27000 times (Fig. 18(b)) (Li et al., 2010, 2012). In addition to extraordinarily high reaction temperatures, processing large-sized feedstock also prolongs reaction time to tens of minutes or even several hours. Therefore, these thermochemical reactions are energy-intensive and have low efficiency and productivity.

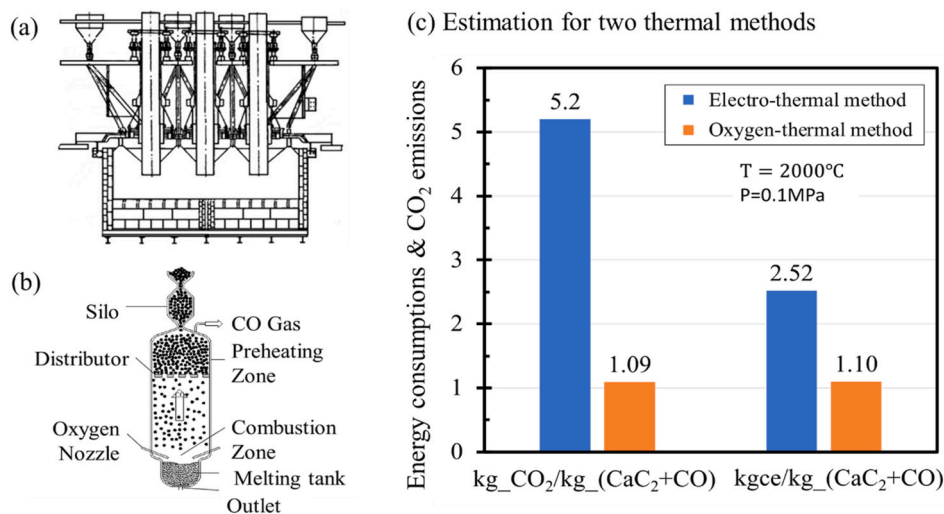


Fig. 17. Illustrations of (a) an electro-arc furnace and (b) a two-stage oxygen-thermal reactor for calcium carbide production, and (c) their estimated energy consumptions and CO_2 emissions for electro-thermal and oxygen-thermal methods (Jin et al., 2022; Shan et al., 2018).

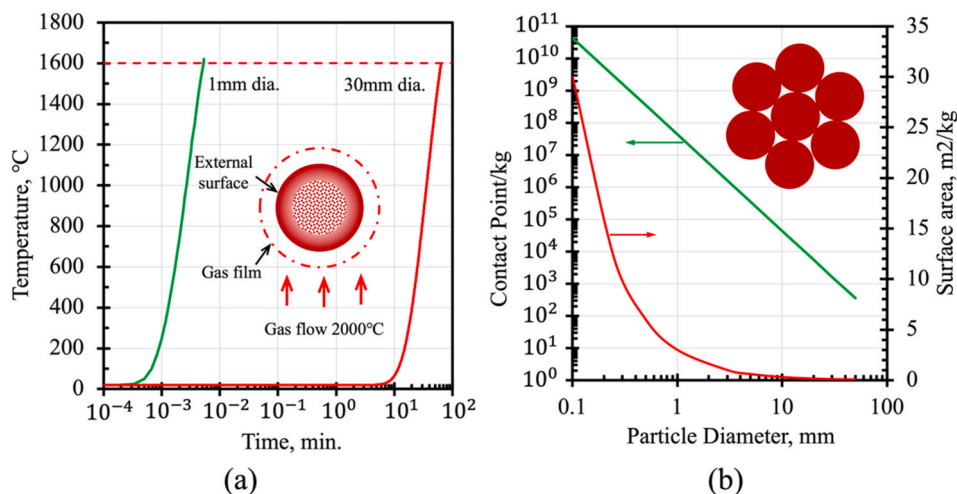


Fig. 18. Effect of particle size on (a) the heating time of a particle and (b) the contact point between particles (Fu et al., 2023a).

Based on our analysis (Fu et al., 2023a), reducing the particle size of raw materials can dramatically improve heat transfer and solids contact in the reactor, thus considerably reducing the reaction temperature and time and increasing energy utilization efficiency, production capacity, and product quality. In this case, it becomes, however, necessary to choose reactor types that are capable of handling small particles.

1) Processing small particles

In demonstrating that processing small particles can significantly reduce reaction temperature and time, we take the solid-state reaction between CaO and C as an example. As shown in Fig. 19, the operating temperature is generally 2000–2300 °C when above 5 mm of particles are used in industrial electric-arc reactors. When the particle size is gradually reduced, the reaction starting temperature becomes lower and closes to the Tammann temperature of CaO (~1300 °C), at which CaO molecular migrations are theoretically significant (Li et al., 2010, 2012).

The sintering of magnesia is another example to demonstrate the effect of particle size on the reaction temperature and time. Highly densified magnesia, often called dead burned magnesia (DBM), has

characteristics of high melting point, good slag resistance, strong corrosion resistance, and high-temperature strength, which are required by many high-temperature applications, such as high-grade refractory materials and various high value-added products. Currently, DBM is prepared by a conventional two-step process, as schematically shown in Fig. 20(a) (Guo, Z. et al., 2020; Guo et al., 2021). In shaft kilns, the sintering process operates at temperatures as high as 1900–2300 °C and takes over 10 h. Despite these harsh operation conditions, the bulk density of produced DBM briquettes is still lower than 3.4 g/cm³, the bulk density that is the lowest threshold required for high-quality DBM products. The thermal energy efficiency of the sintering process is only 30%–45% because of high sintering temperature, long sintering time, high heat loss, and poor heat recovery.

To overcome the issues related to the conventional DBM production process, researchers at the Shenyang University of Chemical Technology have recently reported an advanced fluidized bed process. As schematically illustrated in Fig. 20(b), the new process sinters particles of 0–5 mm in size in a fluidized bed (Fu et al., 2023a), dramatically improving the transfer rates between gas and particles and between the exterior and interior of particles, thereby shortening the sintering time (from 10 h to <5 min) and reducing the sintering temperature (from above 2000 °C to 1500–1600 °C). The DBM products produced are characterized by well-developed crystal structures with a bulk density of close to 3.5 g/cm³, meeting the requirement of high-quality DBM products. This process also remarkably increases production capacity and saves more than 50% energy consumption. In addition, the new process eliminates the pulverization and briquetting steps, thus considerably saving energy and reducing dust emissions.

2) Developing high-temperature fluidized bed reactors

As indicated in the previous two examples, traditional high-temperature reactors (e.g., electric-arc furnaces and shaft kilns) become unsuitable when processing small particles. In most cases, fluidized bed reactors become the best choice because of their well-known advantages, such as high heat and mass transfer rates, uniform temperature profile, and large processing capacity. To illustrate these characteristics further, we discuss three other typical high-temperature thermochemical reactions: cement clinker production, calcination of minerals, and iron reduction.

(a) Cement clinker production

Cement is the main constituent of concrete, the material most widely used in transportation and building industries globally. The cement

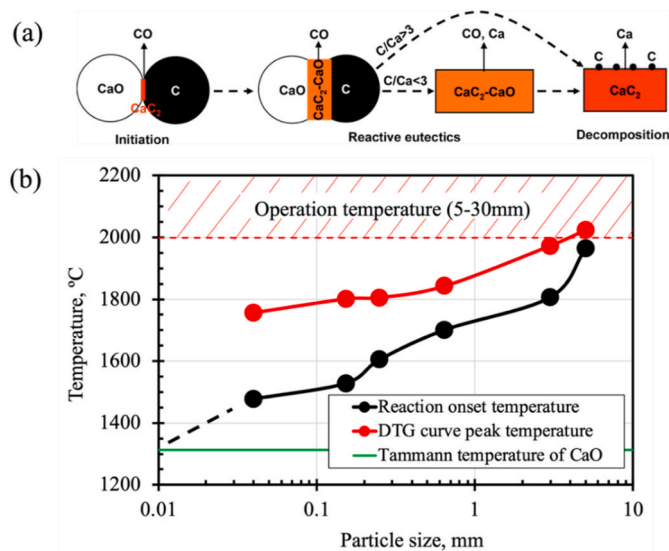


Fig. 19. Illustration of CaC₂ production from CaO and C with (a) reaction process and (b) effect of particle size on reaction temperature (Li et al., 2010, 2012).

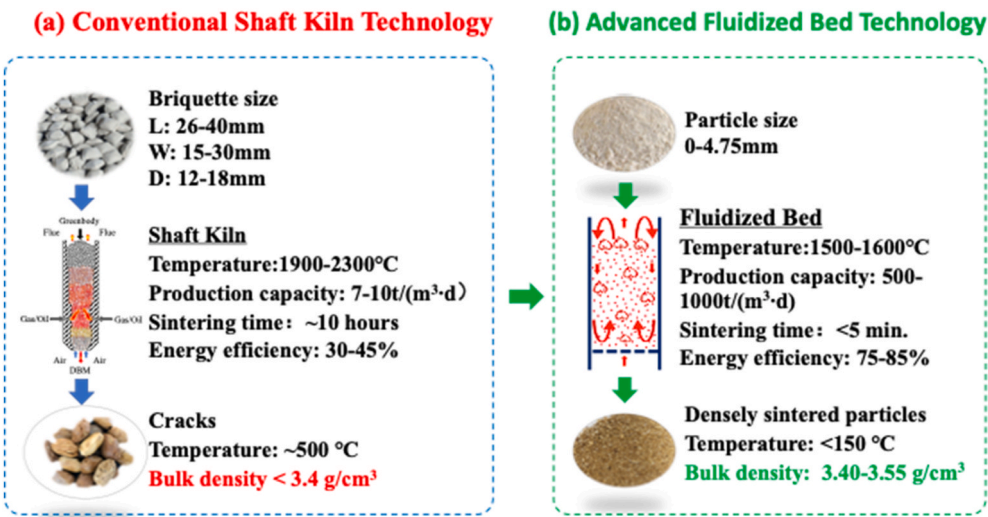


Fig. 20. Comparison between the conventional and advanced two-step processes to produce dead burnt magnesite (Fu et al., 2023a; Guo, Z. et al., 2020).

industry emits approximately 8% of global CO₂ emissions. China, the largest cement producer in the world, produced more than 2.3 billion tons of cement in 2020, which consumed more than 240 million tons of standard coal equivalent and emitted 1.46 billion tons of carbon dioxide (about 40 percent comes from energy consumption).

Currently, the cement clinker is mainly produced in rotary kilns at temperatures of 1800–2000 °C using raw materials of 10–80 mm, despite the minimum calcination temperature of only about 1000 °C. Inside rotary kilns, raw materials are heated dominantly by radiation heat transfer from high-temperature combustion gases, usually characterized by low heat transfer rates. Consequently, rotary kilns used for cement clinker production are typically several meters in diameter and tens of meters in length and have less than 55% of the overall thermal energy efficiency.

The fluidized-bed cement kiln system has been in development since the early 1980s, and a scaled-up test operation of the plant was completed at the end of December 1997 (Hara et al., 1998; Yuko et al.,

2000). As shown in Fig. 21, the raw material particle size in a fluidized bed kiln is as small as 0–4 mm, which significantly promotes the gas-solid heat transfer. The fluidized bed kiln operates at 1300–1400 °C with a thermal efficiency of more than 80%, reducing the energy consumption of cement production by 23–38% compared to rotary kilns. On this basis, we estimate that by using fluidized bed technology, about 130–220 million tons of CO₂ emissions can be reduced in China based on its current annual cement production.

(b) Calcination of minerals

The first step to utilize various ores is calcination of the minerals. The typical examples include productions of lime, magnesite and clay, as the products from calcination of limestone, magnesite and clay minerals, respectively. Some metal oxides are also produced in high amounts through calcination, such as aluminum oxide and magnesite from decomposition of their hydroxides. These materials are indispensable for

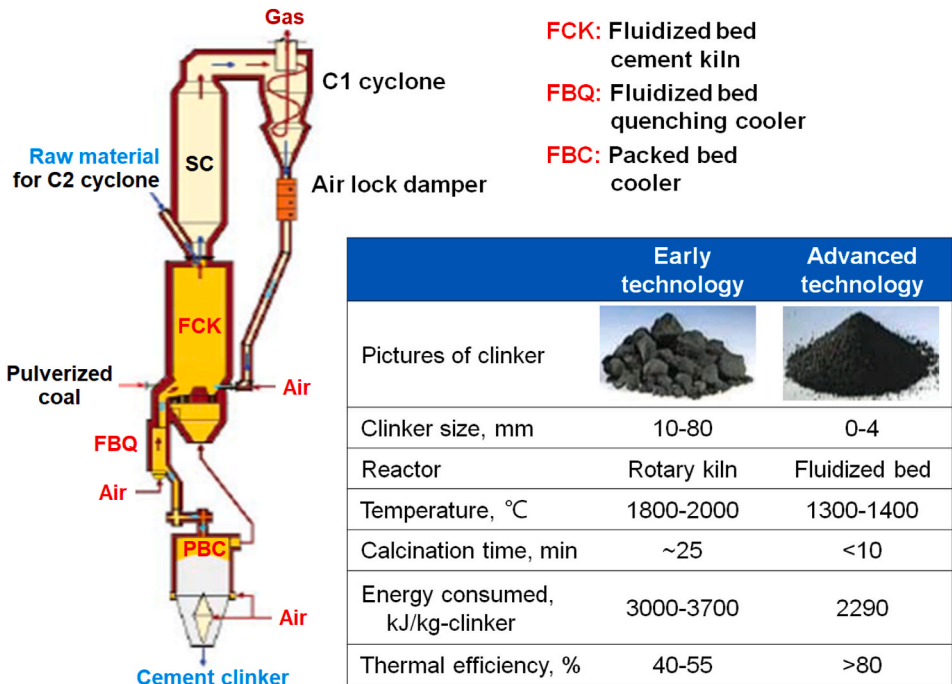


Fig. 21. A schematic of a fluidized bed cement kiln system and its performance comparison with rotary kilns (Hara et al., 1998).

many processes, such as ironmaking, flue gas desulfurization, building material production, and chemical synthesis (Dowling et al., 2015). In 2021, the global productions of lime, aluminum oxide, and magnesia were about 430, 150, and 16 million tons, respectively (Garside, 2023; Zhao et al., 2022). Calcination of minerals is a kind of energy-consuming and CO₂ emission-intensive processes. This is the case especially for carbonate calcinations (lime and magnesia). Taking lime-making as an example, the energy consumption of today's rotary lime kilns is in the range of 5.1–9.3 GJ/ton product (Boateng, 2016; Eriksson et al., 2014), much higher than the theoretical calcination heat of 3.16 GJ per ton CaO. The average CO₂ emission is around 1.2 tons per ton of lime, of which 30–40% is from energy consumption and the rest from the decomposition of raw material limestone (Dowling et al., 2015). Apparently, reducing CO₂ emissions from calcination processes can be achieved by reducing energy consumption (discussed hereafter) and capturing or utilizing CO₂ from carbonate decomposition (discussed in later sections).

Considering lime-making, rotary kilns have been used dominantly in the production of lime (Fig. 22(a)). Conventional rotary lime kilns, with diameters of 1.2–3.3 m and lengths of 22.7–152.5 m (Boateng, 2016), are usually operated at temperatures of 1000–1200 °C, much higher than the calcination starting temperature of 800–900 °C. In conventional rotary kilns, combustion of a gas or coal fuel, with a flame temperature as high as 1800–2000 °C, provides the calcination heat. Product lime is discharged from kilns after raw materials are calcined for 5–10 h (Eriksson et al., 2014). The high operating temperature and long calcination time are mainly attributed to the low heat transfer rate, which is dominated by radiation between high-temperature gases and solid materials and conduction between materials. The use of large-sized raw materials (i.e., 10–60 mm) (Boateng, 2016; Chen, 2013; Eriksson et al., 2014) in rotary kilns is aimed at avoiding materials packing themselves tightly upon rotation and thus keeping the particle bed a better conductor of heat. However, this practice causes an increase in energy consumption and a reduction in production capacity.

Fig. 22(b) shows a schematic of a fluidized bed limestone calciner (Chen, 2013). Processing small particles of 5 mm and below in fluidized beds reduces the complete calcination time to less than 12 min at 950 °C. Thanks to their lower calcination temperature, shorter calcination time, and significantly increased production capacity, fluidized bed limestone calciners increased the energy efficiency to 85% or above. It is estimated that the total annual CO₂ can be reduced to 89 million tons globally and 58 million tons in China based on its current lime production.

Calculation of magnesite is highly similar to that for limestone in

thermochemical process, where magnesite is directly heated using high-temperature flue gas from fuel combustion, and the calcination reaction starts at temperatures of 600–700 °C. Currently, the most widely adopted technologies in calcining Magnesite, for decades, are small-size shaft kilns for which only large-size particles in 30–80 mm are usable as raw feedstock in order maintain a good gas permeability through the bed. Because of the intraparticle heat-transfer limitations, the large-size raw magnesite has to be calcined at ~1100 °C for 3–5 h inside the kilns, causing high energy consumption and low thermal efficiency of about 34% (An et al., 2021). If the particle size is adjusted to 150 µm and below, the decomposition rate of magnesite can reach up to 98% in only 1–3 s at 800–900 °C, as a consequence of the greatly improved gas-solid interactions and intraparticle heat transfer (Sun et al., 2020). On this basis, an advanced process of transport bed flash calcination (Fig. 23(a)) has been developed for granular magnesite to achieve a significantly increased thermal efficiency of ~67% (An et al., 2021). The process is currently being under verification in a demonstration plant with a treatment capacity of 400,000 t/a magnesite (Fig. 23(b)).

(c) Iron reduction

Ironmaking, one of the energy-extensive industrial processes, has been dominated by the traditional blast furnace route, which uses costly lump ore or pellets as raw materials. To reduce material costs and process energy consumption, several new ironmaking developments based on fluidized-bed technology have begun for several decades. The main advantages of fluidized-bed iron reduction technologies are that fine iron ore can be directly charged to the process and be reduced at low temperatures and short reduction times (Schenk, 2011). Fig. 24(a) shows an alternative ironmaking process using a suspension or flash-type furnace, which is actually a downflowing fluidized bed reactor (Vehc, 2010). In this reactor, iron ore concentrates of ~30 µm are reduced at 1300 °C for only a few seconds, reaching 90–99% reduction. Using any of the three possible reductants/fuels, including coal, natural gas, and hydrogen, can save ~38% of energy compared with the blast furnace (Fig. 24(b)). As a result, the technology generates 69%, 39%, and 4% of the carbon dioxide produced in the blast furnace process when coal, natural gas, or hydrogen are used as fuel, respectively. Based on these data, we estimate that without changing the coal fuel, about 400 million tons of CO₂ emissions can still be reduced from ironmaking in China if the fluidized bed reactor replaces the blast furnace process.

Despite the advantages of fluidized beds for processing small

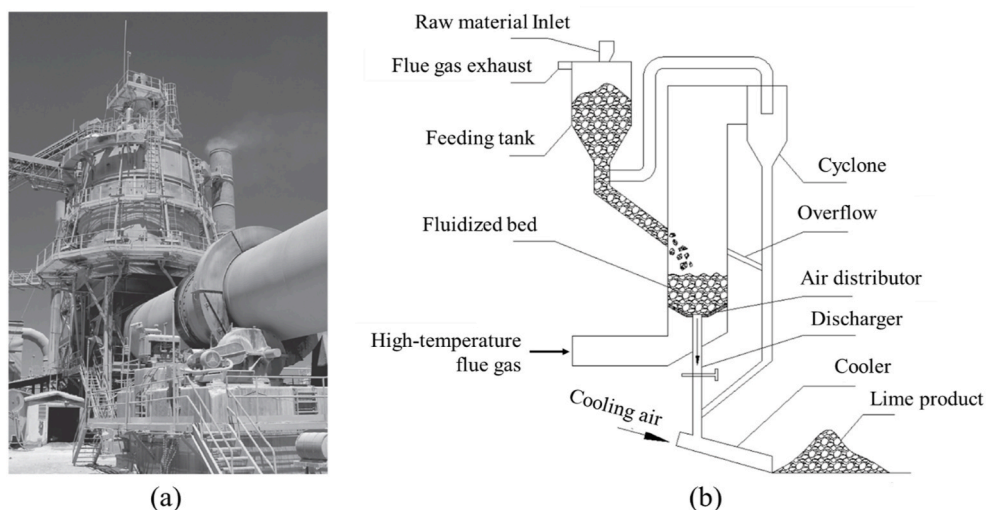


Fig. 22. Illustrations of Lime production with (a) a photograph of an industrial rotary lime kiln (Boateng, 2016) and (b) a schematic of fluidized bed limestone calciner (Chen, 2013).

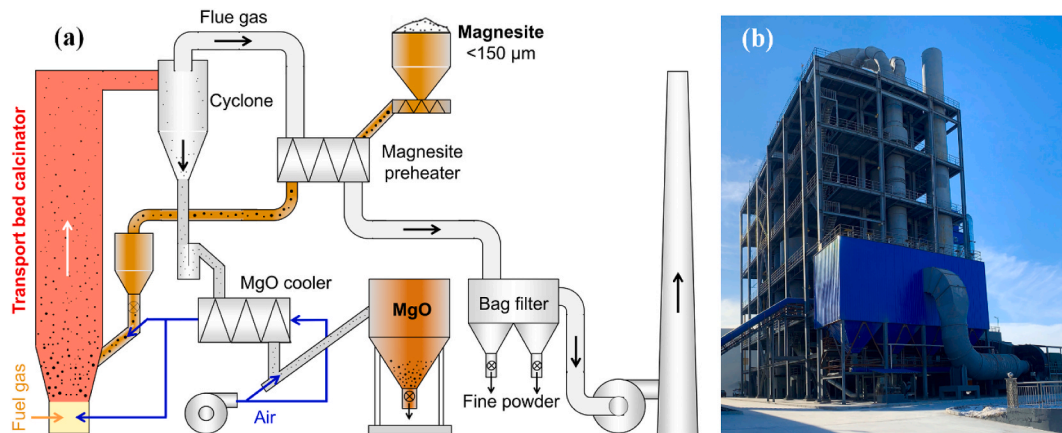


Fig. 23. (a) A schematic of transport bed flash calcination process for granular magnesite and (b) a photograph of a demonstration plant (An et al., 2021).

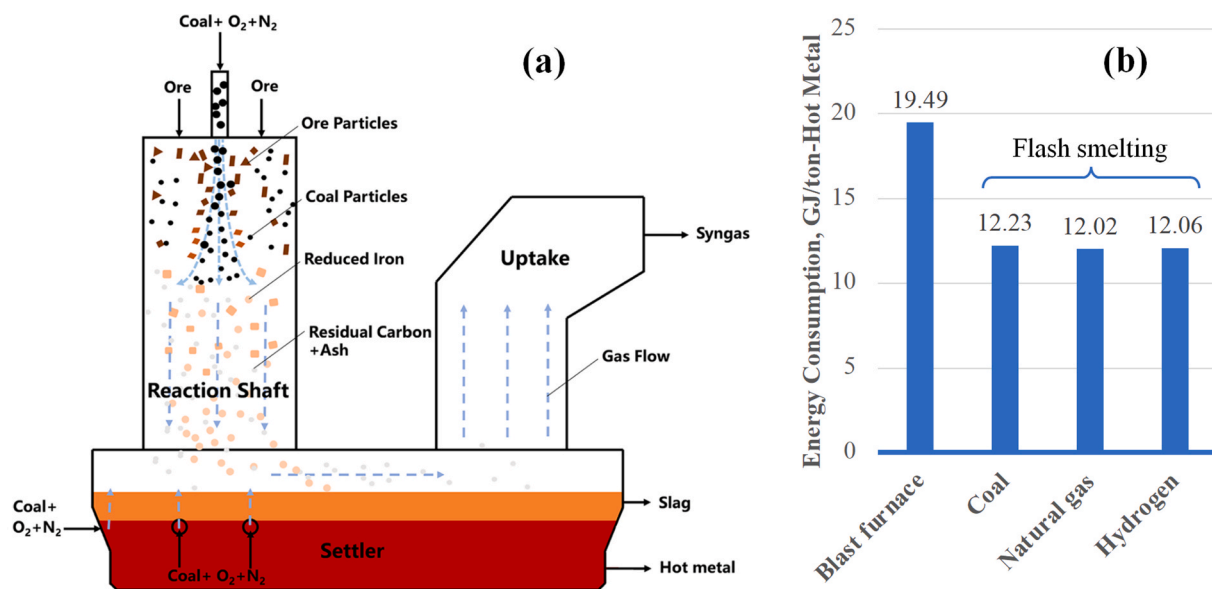


Fig. 24. (a) A schematic of fine iron ore reduction in a downer reactor and (b) energy consumption using coal, natural gas, and hydrogen as fuel (Vehec, 2010).

particles, research further demonstrated that operating at high temperatures presents a considerable risk and challenge in practice (Fu et al., 2022, 2023b). Solid particles at high temperatures will change in thermal, structural, surface, and chemical characteristics due to chemical reactions, softening, agglomeration, sintering, etc., thereby increasing interparticle forces and causing defluidization problems. As a result, high-temperature fluidized beds used to produce cement, lime, and iron powders have not been commercialized because of unresolved technical and practical issues. Continuous research on high-temperature fluidized beds is one of the opportunities for ETC. Besides, special attention is deserved for the potential increase in energy consumption caused by gas cleaning when processing small particles.

4.2. Carbon substitution

In addition to processes that use carbonaceous fuels as energy sources, the carbothermal reduction reaction processes use carbon as the reducing agent to produce metallic materials (e.g., Fe, Si, Ni, Co, Cu, etc.) from their corresponding minerals. Carbon is also needed as a reactant to produce numerous carbides, chemical compounds composed of carbon and metals or semi-metallic elements (e.g., CaC_2 , LiC_2 , SiC , B_4C , Fe_3C , Al_4C_3 , etc.). Because of its excellent electric conductivity, carbon is widely used as electrodes in electrolytic reactors, electric-arc

furnaces, and some electrochemical reactors.

In general, fossil carbonaceous fuels and feedstocks can be substituted with other fossils of low carbon intensity (e.g., oil, gas), carbon-neutral biomass, or even non-carbonaceous ones (e.g., hydrogen). We call these options carbon substitution, a practical yet effective approach to decreasing the carbon intensity of fuels and feedstocks. In principle, there are numerous options for using biomass materials as coal substitutes. But, to be within the scope of this article, we highlight a few thermochemical technologies that we believe are most effective in supporting the carbon substitution strategy.

4.2.1. High-carbon fuel substitution

1) Fuel switching

As stated earlier, the carbon emission intensity of most industrial processes, including electric power generation, industrial heating, ironmaking, production of cement clinker, lime-making, and many other energy-intensive processes, is closely dependent on the fuel used. It is a simple solution to reduce carbon emissions by replacing a fossil fuel of high carbon intensity (e.g., coal) with a substitute fuel of low or zero carbon intensity (e.g., natural gas, organic waste, and biomass) in the same process. For example, as we already indicated in Fig. 24, switching

fuel from coal to natural gas in the ironmaking process can reduce CO₂ emissions by 61% compared to coal-fueled blast furnaces. This simple fuel switching will cut 780 million tons of CO₂ emissions from China's ironmaking industry. Additionally, we estimate that ~900 million tons of CO₂ emissions can be avoided annually in China if approximately 50% of China's agricultural and forestry biomass waste (approximately 500 million dry tons) can be used to replace coal in coal-consuming processes.

2) Cofiring

However, some barriers hinder fuel switching in certain vital processes, for which attaining the process temperature required with another fuel or obtaining the replacement fuel with sustainable supply and affordable costs may be problematic. In many parts of the world, it is risky to rely solely on biomass because its supply is significantly affected by the seasonal nature of biomass resources and supply infrastructure. For this reason, we strongly recommend cofiring that burns a secondary fuel (biomass) with a primary fuel (coal) in the same existing combustion equipment. Cofiring biomass with coal and/or petroleum coke, sometimes known as fuel blending, offers several distinct advantages compared to operations that burn 100% biomass, including lower capital costs, higher efficiency, and increased economies of scale (Basu, 2018; Gil and Rubiera, 2019). It also overcomes corrosion and ash deposition issues caused by normally alkali-rich biomass ash particles. Cofiring allows the combustion of renewable fuel in an existing facility but can change back to coal if biomass is unavailable.

Several biomass and coal cofiring options have been available, including direct, indirect, and parallel cofiring (Gil and Rubiera, 2019). Direct cofiring is the simplest, cheapest, and most widespread method of cofiring biomass with coal in a boiler, but it is limited to around 10% of the biomass ratio due to technical and economic restraints in most cases (Fig. 25(a)). Indirect cofiring involves gasifying the solid biomass in a separate gasifier into syngas and cofiring the syngas in the combustor (Fig. 25(b)). This cofiring option is more complex and expensive, but it allows for a greater variety of biomass types and higher percentages of biomass to be used. Parallel cofiring is similar to indirect cofiring, but the biomass is not first gasified but burned in another boiler (Fig. 25(b)). Due to the required high operating temperatures, both indirect and parallel cofiring operations present certain difficulties and drawbacks, such as slagging, fouling, and corrosion.

To overcome these issues, we propose an alternative indirect cofiring method schematically shown in Fig. 25(c). The new method offers all biomass cofiring advantages with superior performance to traditional

cofiring technologies. It first pyrolyzes the biomass at low temperatures, not gasifying or burning at high temperatures. The pyrolysis gas containing gaseous tar of high reducibility is injected into the upper section of the combustor to serve as a reburning fuel to reduce NO from the coal combustion to harmless N₂. The char is sent to the bottom of the combustor for complete combustion. This way, the issues associated with general indirect and parallel cofiring can be resolved while achieving both cofiring and NO_x reduction purposes. To develop this new technology, the ETC technologies, including pyrolysis, gasification, and combustion, particularly the method of reaction decoupling and restructuring, will be especially useful.

4.2.2. Fossil carbon substitution

Carbon (i.e., coke, activated carbon, graphite, porous carbon, and carbon nanotubes) is widely used in many industrial processes. Most of these carbon materials are produced from fossil carbonaceous materials (e.g., coal, petroleum, or natural gas). To reduce atmospheric CO₂ emissions, these carbon materials, at least in part, can be obtained from plastic pyrolysis under different reaction conditions (Chen et al., 2021). By varying pyrolysis conditions, the yield and characteristics (e.g., pore structure and surface functionality) of the functional carbon materials can be controlled.

Biomass is a renewable and abundant carbon resource. Carbonization of biomass is an effective thermochemical conversion process to produce solid carbon products, i.e., char or charcoal. It is also known as slow pyrolysis, characterized by low heating rates that maximize char yield. The produced bio-carbon, known as biochar or charcoal, can be used in many industrial processes to substitute for fossil carbon reactants (such as reductants), sorbents, or feedstocks, including used for the manufacture of diversified porous bio-carbon materials such as activated carbon. In addition, biochar has great potential to be used as an effective soil amendment to improve the soil's properties and generate a significant carbon reduction, with a certain contribution to the soil's "carbon sink" (Hepburn et al., 2019). China's annual terrestrial carbon sequestration is estimated to be about 1000–1300 million tons of CO₂ (Devasahayam and Strezov, 2018; Ding, 2021), and we believe this capacity can be further enhanced by soil amendment. As the soil's bio-carbon content becomes higher, the growth rate and yield of biomass plants will rise, which creates a positive feedback loop that improves CO₂ absorption through CO₂ photosynthesis. Once the technology is applied to 50% or 500 million tons of the produced agriculture biomass (dry basis), the biochar storage in the soil can potentially reduce more than 500 million tons of CO₂ (Fu et al., 2022).

Currently, various pyrolysis systems are available to produce biochar

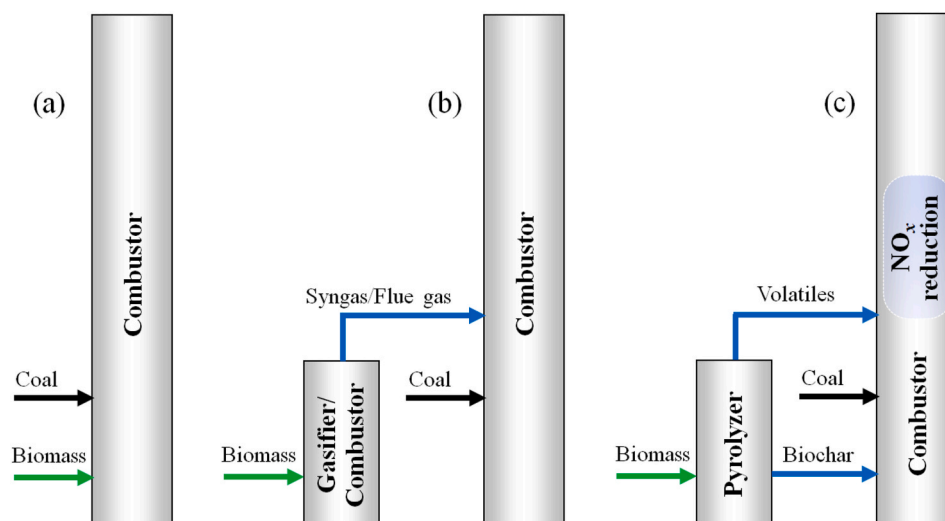


Fig. 25. Schematic presentation of cofiring technology options. (a) direct cofiring, (b) indirect and parallel cofiring, and (c) advanced indirect cofiring.

(Ronsse et al., 2015). However, considering the poor fluidity and growing interest in using biochar for soil amendment, we prefer the slow pyrolysis systems to have the following characteristics: flexible processing capacity, better material handling ability, and continuous operability. In addition, we like the pyrolysis system to be heated by combustion of its own produced pyrolysis gas with either indirect or direct methods. Fig. 26 shows two pyrolysis systems that meet the above criteria. The use of mechanical forces (rotation or screw feeder) to move solid materials ensures that sticky and fibrous materials, regardless of their dimensions, shapes, and cohesiveness, can be processed with significantly reduced risks of blockages and excessive pressure drop.

Finally, we need to note that industrial carbon materials are typically required to provide functional properties and structures to meet the requirements of various applications. Thus, finding a substitute has never been easy, and not all these materials can be easily replaceable by the carbon from the above-described processes. Therefore, more research and engineering developments from the ETC perspective are still needed to make some impossibles possible.

4.2.3. Substitution of hydrogen for carbon

In the long term, the development of alternative technologies that entirely replace carbon with hydrogen in processes such as ironmaking, MG-Si production, and many other reduction processes of mineral materials is the most effective to reduce carbon emissions. The potential of using green hydrogen as a reducing agent can be explained by iron and steel manufacturing, a globally well-known energy-consuming and carbon-emission industry that emits about 27% of the CO₂ of the global manufacturing sectors today (Hasanbeigi et al., 2014). As shown in Fig. 24, the substitution of hydrogen for coal in the ironmaking process can reduce CO₂ emissions by 96% compared to coal-fueled blast furnaces, which will lead to ~1240 million tons of CO₂ emission reduction from China's ironmaking industry.

However, the direct reduction of iron using H₂ has many technical and practical challenges (Hasanbeigi et al., 2014; Spreitzer and Schenk, 2019). Iron particles are prone to sticking and fusion in a reducing environment, making stable and durable operation difficult (Guo, L. et al., 2020). Production of hydrogen to meet the massive demand and operating hydrogen supply, storage, and safe operation require

unprecedented efforts. For this reason, ETC is undoubtedly expected to play a crucial role in making it a possibility.

4.3. Carbon recycling

Ultimately, establishing a carbon-neutral society requires carbon or carbon-based material to form a circular utilization paradigm. However, with few exceptions, almost every natural and synthetic material will become non-usable after several repeated recycled uses because the material has lost its characteristics or degraded in quality. The reason is that in conventional recycling, the discarded materials are mechanically recovered and physically processed for manufacturing products that require lower quality. When carbon-based materials become physically or mechanically non-recyclable, they can always be recycled at the molecular level, known as chemical recycling. Chemical recycling provides a sustainable solution to reuse the molecules of materials. In terms of carbon, we call this chemical recycling in this article "Carbon recycling". It refers to technologies that utilize carbon from biomass or fossil-origin wastes (e.g., polymer wastes, CO₂, etc.) as feedstock to produce synthetic C-materials and C-chemicals, wherein special emphasis is placed on carbon reuse, if here excluding the storage of carbon such as biochar into soil to form substantial carbon sink.

Thermochemical conversion technologies play a critical role in carbon recycling. As conceptually illustrated in Fig. 27, thermochemical technologies can be used to recycle a wide range of organic and inorganic materials, such as plastics, rubber, petroleum residues, construction and demolition debris, agricultural and forestry biomass, landfill gas, coal mine gas, cement, coal ash, and many others. In theory, it is possible that thermochemical technologies can decouple material manufacturing from fossil resource extraction to prevent fossil resources from further depletion. From the aspect of carbon recycling, the reuse of discarded carbon-based materials enables the direct reduction of carbon emissions. Eventually, thermochemical recycling provides an opportunity to close the material cycle. This work shows a few examples below to demonstrate how ETC plays a crucial role in promoting carbon recycling.

4.3.1. Chemical recycling plastic waste to crude oil

Plastics are prevalently used worldwide for packaging, construction, textiles, electricals, transportation, etc. Global plastic production has been rising over the years, reaching ~370 million metric tons in 2019 (Chen et al., 2021). Plastic products, such as packaging bags, usually have a relatively short service life. Generally, over 80% of the total plastic production becomes waste, of which only ~10% are recycled, and the remainder follows a linear economy model: disposal or incineration. Therefore, management of plastic waste has been an enormous challenge.

Thermochemical conversion of plastic wastes into liquid fuel as a crude substitute is one of the most effective ways to address the challenges of plastic waste management. Simultaneously, it helps transform the petroleum industry into a more sustainable circularity with reduced dependence on fossil crude. Currently, there are several thermal catalytic technologies reported for plastic conversion to gaseous and liquid fuels (Chen et al., 2021; Kunwar et al., 2016; Li et al., 2022). To maximize liquid oil yield or higher boiling point hydrocarbons, pyrolysis reactors must be capable of quickly releasing and limiting the deep decomposition of high-molecular volatiles. Fig. 28(a) shows such a pyrolysis reactor conceptually (Lai et al., 2015; Zhang et al., 2014). In this reactor, raw material particles are heated near the outer wall when they move down by gravity. The bed particle temperature decreases gradually from the wall to the center. After the volatiles are released in the high-temperature area near the wall, they flow through the particle layer along the direction of temperature declination to the central internals, where gaseous products are collected and quickly withdrawn from the reactor. In this configuration, the secondary cracking reactions between volatilized primary products are significantly reduced so that

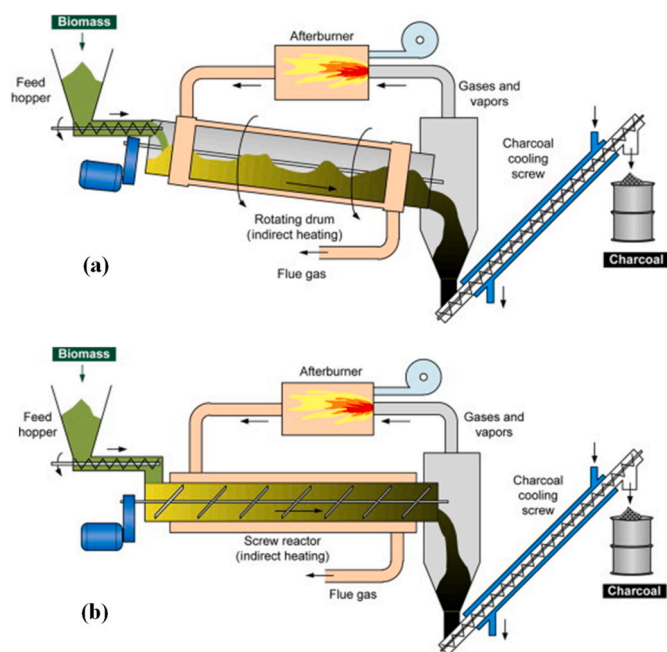


Fig. 26. Schematics of (a) an indirectly heated rotary retort and (b) an indirectly heated screw auger reactor to produce charcoal (Ronsse et al., 2015).

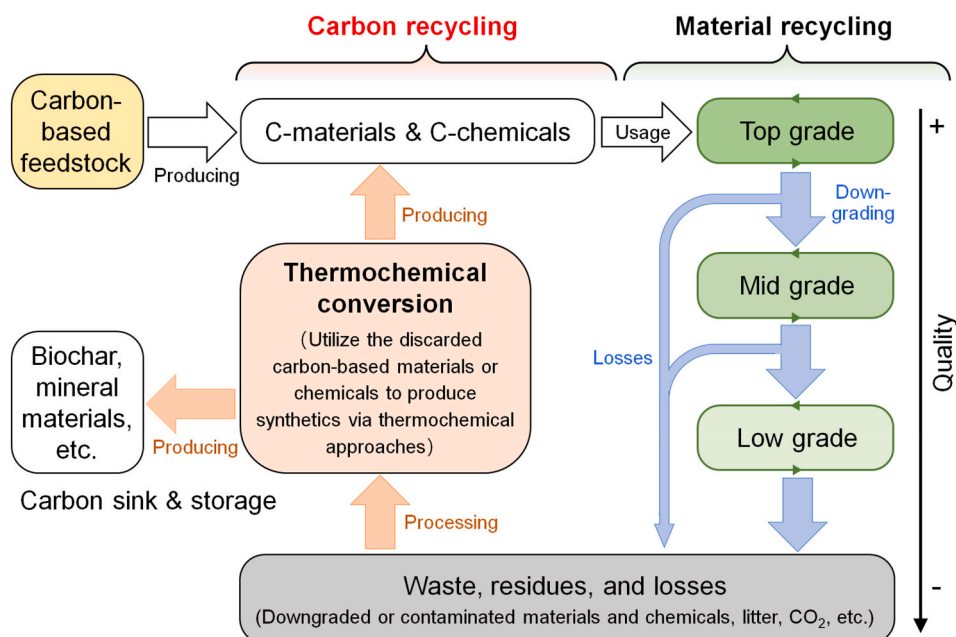


Fig. 27. Conceptual illustration of carbon recycling and material recycling.

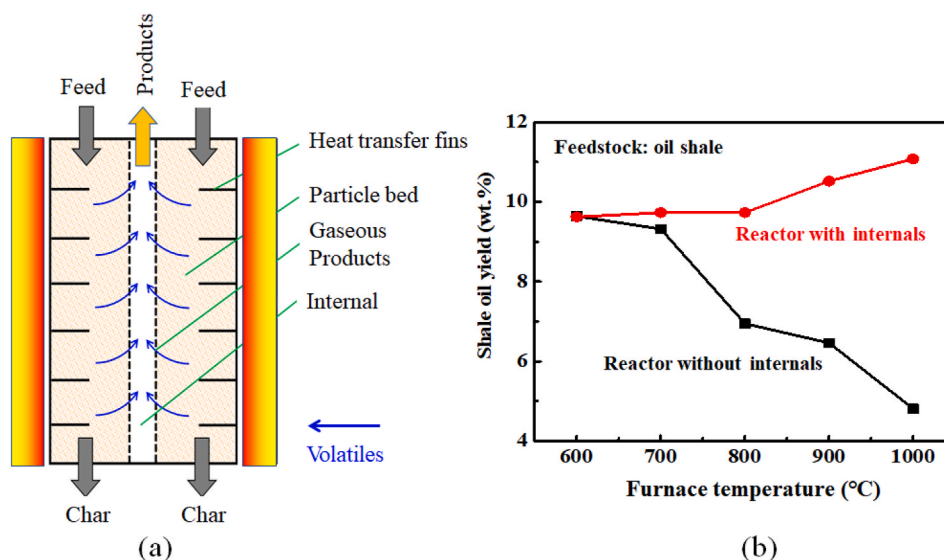


Fig. 28. (a) A process diagram of an internals-assisted moving bed pyrolyzer, and (b) the comparison of oil yield with pyrolysis temperature between reactors with and without internals (Lin et al., 2015).

the oil yield in the final product is not only high but also increases with the increase of pyrolysis temperature, which is opposite to the reactors without internals (Fig. 28(b)).

Other thermochemical technologies, such as fluidized bed (Kaminsky, 2021) and catalytic pyrolysis (Chen et al., 2021), can also be adapted based on feedstock characteristics and targeted products. These technologies can generally produce a gas product with 75–80% of oil yield. Besides, various renewable and abundant biomass materials can also be utilized for chemical or fuel production. The co-pyrolysis of plastic and biomass is a beneficial strategy to improve the quality of gas or liquid fuels possibly. It is worth pointing out that when biomass wastes are co-pyrolyzed, the liquid oil may be hard to use as petroleum feedstock because it generally contains too high oxygen.

Besides, plastic waste can be converted to chemical monomers and other desired molecules using existing thermochemical conversion infrastructures such as thermal crackers. For each plastic feed, the

operating conditions (i.e., the severity of operation) can be optimized for the formation of desired molecules. Research has indicated that switching the feedstock from virgin fossil fuels to plastic waste is technically feasible but may or may not be economically justified depending on subsequent processing steps and end-product values (Thunman et al., 2019).

China produces about 90 million tons of plastic waste and 60 million tons of petroleum residue annually, which can be thermally degraded to yield ~70 million tons of oil as a crude substitute. Equivalently, this reduces 220 million tons of CO₂ emissions a year.

4.3.2. Chemical recycling CO₂ to mineral materials

As we all know, most CO₂ is emitted from processes that use fossil mineral materials (coal, natural gas, petroleum, carbonates). The emitted CO₂, once captured, can be chemically reversed back to minerals via artificially controllable chemical reactions, known as carbon

mineralization. It is akin to the natural weathering process, in which rocks and minerals with high magnesium (Mg), calcium (Ca), or iron (Fe) content react with CO_2 in the atmosphere to form a stable and inert carbonate rock. The rates of natural mineralization reactions are too slow to be industrially viable for the capture and storage of CO_2 . This is where ETC can help make the mineralization reactions practical by significantly accelerating their kinetic rates. Fig. 29(a) shows a schematic of a fluidized bed of activated serpentinite particles, a versatile mineral family rich in Mg silicate, used for CO_2 mineralization. The experimental results show that the mineral and CO_2 conversions increase with the bed temperature (Fig. 29(b)), and it is feasible to develop an effective CO_2 capture and sequestration process using fluidized bed reactors to process mineralization.

The conversion of carbon dioxide to mineral materials also provides an efficient method for the management of solid wastes, such as byproducts of coal combustion (ash), end-of-life cement, red mud, and many other solid wastes containing alkali or alkaline earth elements. According to our estimations, all these solid waste materials can be remineralized to store 15–90 million tons of CO_2 annually.

4.3.3. Chemical recycling CO_2 to chemicals

There are three main approaches for carbon capture from CO_2 emission sources: pre-combustion capture, in-combustion capture, and post-combustion capture (Breeze, 2015; Hepburn et al., 2019; Miller, 2017). From the perspective of engineering thermochemistry, we focus on thermochemical technologies that facilitate carbon capture or in-situ conversion because they can avoid the process of carbon separation required by the other technologies.

1) Oxy-fuel approaches

To make CO_2 separation easy, in-combustion capture technologies, including mainly oxy-fuel combustion and chemical looping combustion, have been investigated in recent years. In oxy-fuel combustion (Zheng, 2011), the fuel is combusted in the presence of oxygen and CO_2 to ensure that the combustion flue gas contains mainly CO_2 and water. In this way, CO_2 can be readily recovered through condensation. The main problem with this method is that it requires high purity of oxygen, which is usually made by expensive air separation units. In this sense, oxy-fuel combustion uses oxygen separation to replace carbon dioxide separation applied to pre- and post-combustion CO_2 -capture processes. Oxy-fuel combustion can also be applied to the calcination processes of carbonate minerals, such as limestone, magnesite, siderite, dolomite, rhodochrosite, smithsonite, cerussite, strontianite, and many others. Oxy-fuel calcination can produce a highly pure CO_2 gas stream suitable for manufacturing various value-added products. Research has demonstrated that oxy-fuel calcination (Eriksson et al., 2014) of lime in rotary

kilns can produce a high-quality lime product with a reduced specific energy consumption and, thereby, a lower specific carbon dioxide emission.

Based on IGCC, the pre-combustion capture system needs to extract large amounts of steam from the power block for the shift reactor and CO_2 capture unit, leading to a significantly decreased gross power output in comparison with the conventional IGCC without CO_2 capture. Through combining the oxy-fuel technology and IGCC, a novel oxy-fuel IGCC process (Oki et al., 2011) has been proposed to involve the uses of oxygen and recycled CO_2 as a temperature moderator as well as a reaction agent in gasifier and gas turbine combustor. Because the exhaust gas is mainly composed of CO_2 , this system does not require a shift reactor and a CO_2 capture unit. The oxy-fuel IGCC thus simplifies the process configuration, thereby improving the system performance for a net thermal efficiency above 42% based on HHV and a nearly 100% carbon capture rate (Ishii et al., 2019; Oki et al., 2017). As a critical process in oxy-fuel IGCC, the O_2/CO_2 -blown gasification (known as oxy-fuel gasification) has been widely examined in recent years (Long et al., 2020; Spiegl et al., 2020, 2021). Noticeably, it may be a very promising route to recycle CO_2 when the product gas is used as a syngas.

2) Chemical looping combustion

Chemical looping combustion is an alternative form of oxyfuel combustion under development. The process requires two reactors: an air reactor and a fuel reactor. In the air reactor, the oxygen carrier is heated in the presence of air to capture oxygen from air preferentially. The oxygen carrier is then transferred to the fuel reactor, reacting with fuel and returning to the reduced state. The reduced oxygen carrier is recirculated to the air reactor for oxidizing again to form a complete chemical looping. In principle, the chemical looping combustion has the potential for 100% CO_2 capture (Adánez et al., 2018; Zhao et al., 2020), but due to the lack of durable oxygen carriers, the technology is still in an early stage of development.

3) Indirect heating calcination

Fig. 30 shows a novel concept of an indirectly heated reactor for magnesite calcination. In the vertical reactor, finely pulverized magnesite particles are calcined at a low temperature of $\sim 760^\circ\text{C}$ with a residence time of $< 10\text{ s}$ to produce a superior, highly reactive MgO product (Keeling et al., 2019). The reactor is heated by heat transferred through the tube wall, and the evolved CO_2 is captured after the carrier stream is recovered by condensation. With such approaches, we estimate that up to 260 million tons of high-purity CO_2 can be collected annually from China's limestone and magnesite calcination processes.

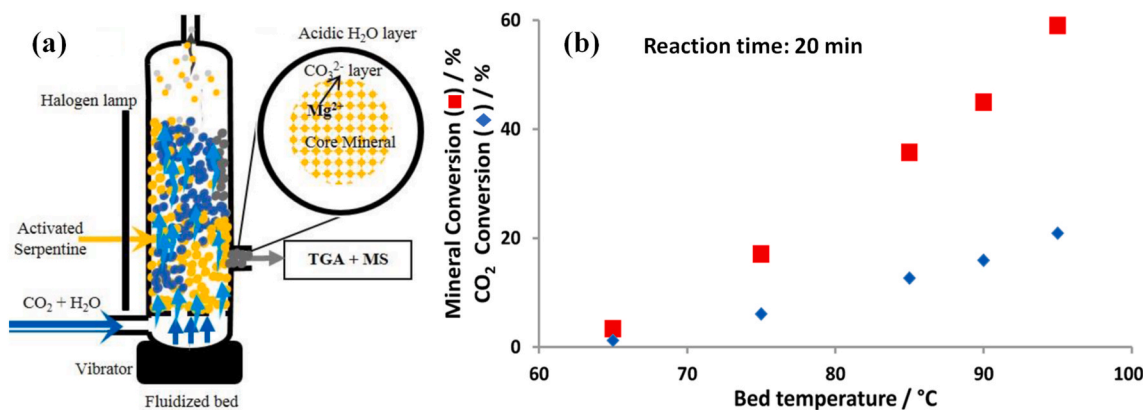


Fig. 29. (a) A schematic of a fluidized bed of activated serpentinite particles for CO_2 mineralization and (b) the effect of reaction temperature on reaction performance (Bhardwaj et al., 2016).

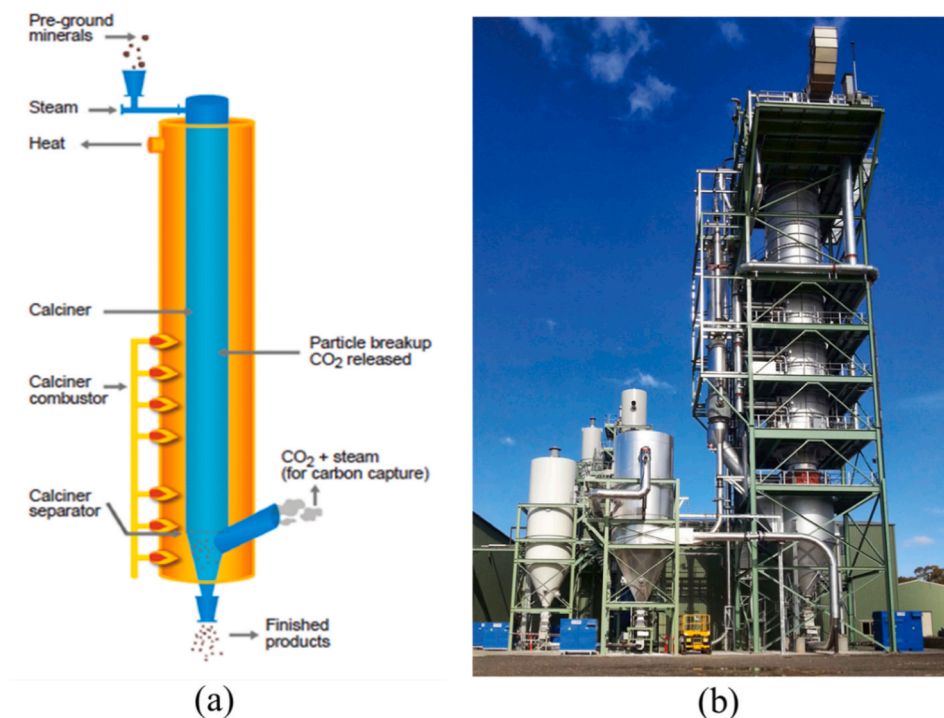


Fig. 30. (a) A diagram of an externally heated fluidized bed calciner and (b) a photograph of the commercial-scale demonstration plant (Keeling et al., 2019).

4) Reductive calcination of carbonates

The reductive decomposition of carbonates is a technology that directly hydrogenates the carbon dioxide produced in the calcination of inorganic carbonates (Baldauf-Sommerbauer et al., 2016; Devasahayam and Strezov, 2018; Lux et al., 2018, 2019). Generally, carbon dioxide hydrogenation technology undergoes two steps: separate and capture CO_2 from the gas stream containing CO_2 and catalytically react CO_2 with hydrogen in a separate reactor to produce synthetic gases and/or chemicals. In contrast, reductive calcination completes the hydrogenation of carbon dioxide in the process of carbonate decomposition (Bruckner et al., 2022; Shan et al., 2018), as exemplified in Fig. 31(a) (Baldauf-Sommerbauer et al., 2016). The reducing agent, which is

hydrogen, is preferably from renewable sources (e.g., solar, wind, hydro, and biomass). In this case, the reductive calcination of inorganic carbonates is not only a method of direct utilization of CO_2 but also a means of hydrogen storage. Accordingly, a closed CO_2 circular can be established by integrating the reductive calcination of carbonates and the recarbonation of metal oxides (Fig. 31(b)) (Lux et al., 2018).

Research has demonstrated that direct hydrogenation can effectively reduce the decomposition temperature of carbonates, a beneficial attribute leading to an additional increase in the energy efficiency of the calcination process. If this novel technology is implemented industrially, we can convert 260 million tons of CO_2 directly to chemicals annually in China, thereby avoiding the CO_2 capture applied for indirect-heating calcination, as discussed above.

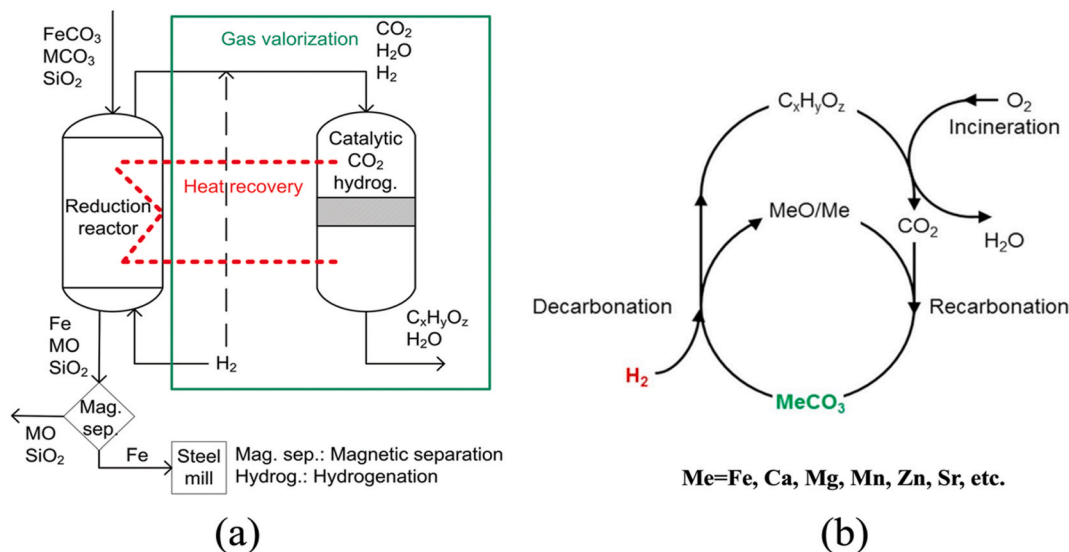


Fig. 31. Process principle for (a) the reductive siderite calcination integrated with catalytic methanation (Baldauf-Sommerbauer et al., 2016), and (b) a closed CO_2 circuit based on the decarbonization of carbonates (MeCO_3) and recarbonation of MeO (Lux et al., 2018).

4.3.4. Chemical recycling CO₂ to geological substances

Once carbon dioxide is captured, it can be used or stored in various ways (Breeze, 2015; Miller, 2017), including sequestration into different possible geological and ocean seams. This kind of carbon storage would have great potential, but it is challenging depending on many uncertain factors. As far as carbon super-emitters mentioned above are concerned, our emphasis for carbon sequestration is placed on applying ETC approaches to help carbonize carbonaceous materials to produce carbon or carbon-rich particles for storage because storing carbon directly is the ultimate strategic option to realize carbon neutrality. ETC can help simulate these reactions in laboratories, revealing and understanding the mechanism and behavior of thermochemical reactions occurring under mimicked underground high-pressure and high-temperature conditions.

5. Conclusion and future perspectives

In this study, we have analyzed the CO₂ emission data from various sources to show that most anthropogenic CO₂ is emitted from a few super-emitters, including the processes of coal-fired power generation, coal-fired industrial heating, iron- and steel-making, non-ferrous metallurgy, cement production, and lime production. All these CO₂ super-emitting processes are based on heat-induced or heat-driven thermochemical reactions, such as combustion, coking, reduction, decomposition, synthesis, and so on. Because these energy- and carbon-intensive processes are practiced in many different industries and deal with fundamentals in a variety of natural science areas, there is an urgent need for a cross-industrial and interdisciplinary science to guide the fundamental research and technological innovation as well as engineering of heat-induced and/or heat-driven thermochemical reactions, thereby providing scientifically sound and practically deployable approaches to reducing CO₂ emissions effectively, substantially, and sustainably.

Engineering Thermochemistry has been proposed as an emerging interdisciplinary science and technology to meet the need for discovering, studying, innovating, and engineering heat-induced and/or heat-driven thermochemical reactions. It is the powerful tool required to deal with CO₂ emissions from those super-emitters. By applying the principles of ETC, we have identified the following approaches to improve energy utilization efficiency and reduce emissions of fossil carbon from

those CO₂ super-emitters.

- 1) Carbon emission reduction
 - Improve coal-fired power generation efficiency
 - Improve coal-fired industrial/rural process efficiency
 - Replacing electrical heating with direct heating
 - Reducing reaction temperature and time
- 2) Carbon substitution
 - Reducing the carbon intensity of fuels/reactants
 - Substituting renewable carbon for fossil carbon
 - Switching to non-carbon fuels/reactants such as hydrogen
- 3) Carbon recycling
 - Accelerated mineralization
 - Capture and conversion of CO₂
 - Storage of carbon (biochar) for soil amendment
 - Carbon sequestration

Adapting to the technological realities, we have conducted a comprehensive analysis of the CO₂ emission reduction potentials using the above ETC approaches. It shows that ETC approaches can potentially reduce around 5 to 6 billion tons of CO₂ emissions annually from the basis of 2020. Combined with the estimated land and ocean carbon sink potentials (Ding, 2021), ETC provides the great opportunity to bring carbon emissions close to the neutrality target in China, as is schematically summarized in Fig. 32.

Finally, it is worth noting that we must take a systematic approach to address the issues related to energy use and CO₂ emissions because no single technology will provide an adequate solution. Transformation to low- and/or zero-carbon processes and products require the efforts of the entire society. Scientific and technological breakthroughs are urgently needed to resolve issues and barriers confronted by emerging technologies of carbon emission reduction, carbon substitution, and carbon recycling. Government policy and financial support should be directed to research, development, and deployment of these emerging technologies to reduce CO₂ emissions from the identified super-emitters effectively and economically. The core is to innovate and even revolutionize the related thermochemical reactions and their engineering technologies. For this, ETC will doubtlessly play a vital and irreplaceable role in the path toward carbon neutrality.

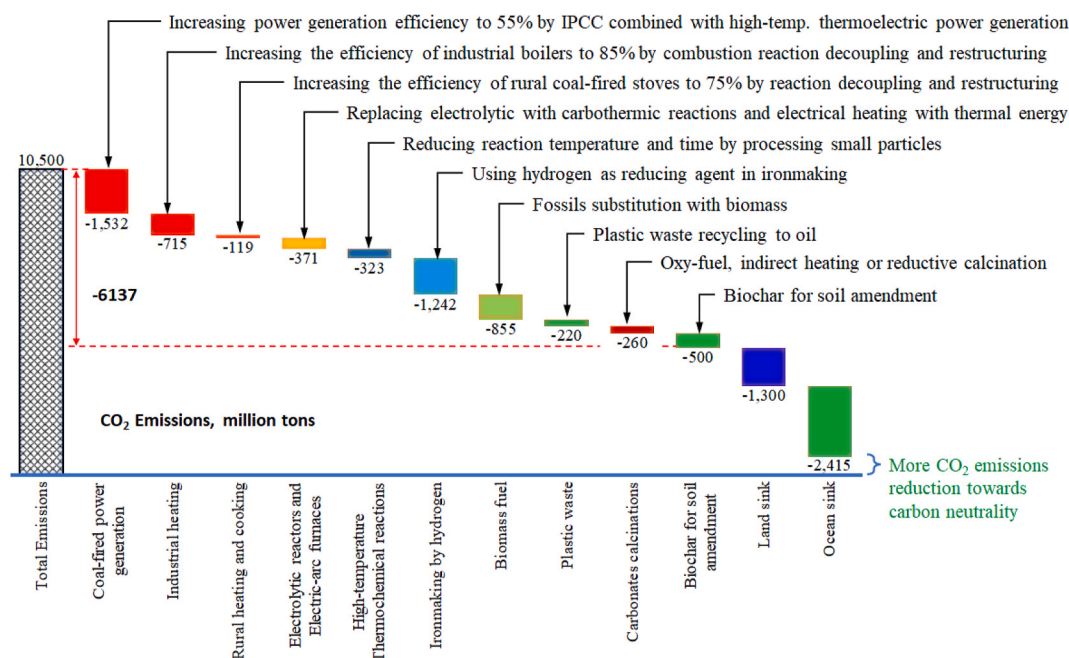


Fig. 32. The estimated CO₂ reduction potentials by the indicated ETC approaches.

Author declaration

We confirm that this manuscript has been read and approved by all authors named. We further confirm that the order of authors listed in the manuscript has been approved by all of us. We understand that the Corresponding Author is the sole contact for all the editorial process.

CRedit authorship contribution statement

Zhennan Han: Conceptualization, Investigation, Visualization, Writing – original draft. **Xin Jia:** Data curation, Formal analysis, Investigation. **Xingfei Song:** Formal analysis, Investigation, Visualization. **Ping An:** Data curation, Validation. **Liangliang Fu:** Data curation, Investigation. **Junrong Yue:** Formal analysis, Investigation. **Jian Yu:** Formal analysis, Investigation. **Xuejing Liu:** Investigation, Visualization. **Zhanguo Zhang:** Methodology, Validation. **Yong Jin:** Data curation, Writing – review & editing. **Mingyuan He:** Writing – review & editing. **Dingrong Bai:** Data curation, Methodology, Visualization, Writing – original draft. **Guangwen Xu:** Conceptualization, Methodology, Funding acquisition, 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.

Acknowledgment

This work was partially supported by the National Natural Science Foundation of China (U1908201, 22242018), the Ministry of Science and Technology of People's Republic of China (2018YFF01011400), and the Natural Science Foundation of Liaoning Province of China (2021-NLTS-12-09).

References

- Adán, J., Abad, A., Mendiara, T., Gayán, P., de Diego, L.F., García-Labiano, F., 2018. Chemical looping combustion of solid fuels. *Prog. Energy Combust. Sci.* 65, 6–66.
- An, P., Han, Z., Wang, K., Cheng, J., Guan, G., 2021. Energy-saving strategy for a transport bed flash calcination process applied to magnesite. *Carbon Resour. Convers.* 4 (1), 122–131.
- Baldauf-Sommerbauer, G., Lux, S., Siebenhofer, M., 2016. Sustainable iron production from mineral iron carbonate and hydrogen. *Green Chem.* 18 (23), 6255–6265.
- Basu, P., 2018. Chapter 11-Biomass combustion and cofiring. In: Basu, P. (Ed.), *Biomass Gasification, Pyrolysis and Torrefaction*, third ed. Academic Press, pp. 393–413.
- Bharath, G., Hai, A., Rambabu, K., Haija, M.A., Banat, F., 2023. Sustainable electrochemical process for recovery of metal ions in synthetic mining wastewater and their utilization in photocathodic CO₂ reduction into formic acid. *Resour. Conserv. Recycl.* 190, 106778.
- Bhardwaj, R., van Ommen, J.R., Nugteren, H.W., Geerlings, H., 2016. Accelerating natural CO₂ mineralization in a fluidized bed. *Ind. Eng. Chem. Res.* 55 (11), 2946–2951.
- Boateng, A.A., 2016. Rotary kiln minerals process applications. In: Boateng, A.A. (Ed.), *Rotary Kilns*. Butterworth-Heinemann, pp. 231–264.
- Bp, 2023. BP Statistical review of world energy. <https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html>. (Accessed 14 April 2023).
- Breeze, P., 2015. Chapter 7-Carbon capture and storage. In: Breeze, P. (Ed.), *Coal-fired Generation*. Elsevier, pp. 73–86.
- Bruckner, B., Hubacek, K., Shan, Y., Zhong, H., Feng, K., 2022. Impacts of poverty alleviation on national and global carbon emissions. *Nat. Sustain.* 5 (4), 311–320.
- Bruno, M.J., 2003. Aluminum carbothermic technology comparison to Hall-Heroult process. *MS Light Metals* 395–400.
- CEADs (Carbon Emission Accounts & Datasets), 2022a. China CO₂ inventory 1997–2019 (IPCC sectoral emissions). <https://www.ceads.net/user/index.php?id=284&lang=en>. (Accessed 14 April 2023).
- CEADs (Carbon Emission Accounts & Datasets), 2022b. China energy inventory 1997–2019 (Apparent Emissions). <https://www.ceads.net/user/index.php?id=133&lang=en>. (Accessed 14 April 2023).
- CEC (China Electricity Council), 2022. China electric power industry annual development report 2021. <https://www.seetao.com/details/96230.html>. (Accessed 14 April 2023).
- Chen, H., 2013. Research on the Calcination Characteristics of Medium-Sized Limestone: A Thesis Submitted for the Degree of Master of Engineering. Huazhong University of Science and Technology, China (in Chinese). <https://cdmd.cnki.com.cn/Article/CDMD-10487-1014025935.htm>.
- Chen, X., Wang, Y., Zhang, L., 2021. Recent progress in the chemical upcycling of plastic wastes. *ChemSusChem* 14 (19), 4137–4151.
- Cochran, C.N., 2016. Alternate smelting processes for aluminum. In: Bearne, G., Dupuis, M., Tarcy, G. (Eds.), *Essential Readings in Light Metals*. Springer, Cham, pp. 1056–1069.
- Devasahayam, S., Strezov, V., 2018. Thermal decomposition of magnesium carbonate with biomass and plastic wastes for simultaneous production of hydrogen and carbon avoidance. *J. Clean. Prod.* 174, 1089–1095.
- Ding, Z., 2021. Research on the framework roadmap for carbon neutrality in China. *China Ind. Inf. Technol.* 8, 54–61. <https://doi.org/10.19609/j.cnki.cn10-1299/f.2021.08.007> (in Chinese).
- Dowling, A., O'Dwyer, J., Adley, C.C., 2015. Lime in the limelight. *J. Clean. Prod.* 92, 13–22.
- Eriksson, M., Hökfors, B., Backman, R., 2014. Oxyfuel combustion in rotary kiln lime production. *Energy Sci. Eng.* 2 (4), 204–215.
- Faddouli, A., Hajji, M., Fadili, S., Hartiti, B., Labrim, H., Habchi, A., 2023. A comprehensive review of solar, thermal, photovoltaic, and thermoelectric hybrid systems for heating and power generation. *Int. J. Green Energy* 1–35. <https://doi.org/10.1080/15435075.2023.2196340>.
- Friedlingstein, P., O'Sullivan, M., Jones, M.W., Andrew, R.M., Zaehle, S., 2020. Global carbon budget 2020. *Earth Syst. Sci. Data* 12 (4), 3269–3340.
- Fu, L., Bai, H., Bai, D., Xu, G., 2022. Hydrodynamics of gas-solid fluidization at ultra-high temperatures. *Powder Technol.* 406, 117552.
- Fu, L., Yue, J., Liu, W., Han, Z., Bai, D., Xu, G., 2023a. Analysis and experiment of sintering and densification of magnesia particles. *Chem. Eng. Sci.* 268, 118396.
- Fu, L., Zhang, Q., Xu, G., Bai, D., 2023b. Pressure fluctuations in a gas-solid fluidized bed at temperatures up to 1650 °C. *Chem. Eng. J.* 468, 143806.
- Garside, M., 2023. Lime production by country in 2022. <https://www.statista.com/statistics/657049/production-of-lime-worldwide/>. (Accessed 14 April 2023).
- Gil, M.V., Rubiera, F., 2019. Coal and biomass cofiring: fundamentals and future trends. In: Suárez-Ruiz, I., Díez, M.A., Rubiera, F. (Eds.), *New Trends in Coal Conversion*. Woodhead Publishing, pp. 117–140.
- Govindan, B., Madhu, R., Abu Haija, M., Kusmartsev, F.V., Banat, F., 2022. Pd-decorated 2D MXene (2D Ti₃C₂Te₂) as a high-performance electrocatalyst for reduction of carbon dioxide into fuels toward climate change mitigation. *Catalysts* 12 (10), 1180.
- Guene Lougou, B., Shuai, Y., Zhang, H., Ahouannou, C., Zhao, J., Kounouhewa, B.B., Tan, H., 2020. Thermochemical CO₂ reduction over NiFe₂O₄/alumina filled reactor heated by high-flux solar simulator. *Energy* 197, 117267.
- Guo, L., Bao, Q., Gao, J., Zhu, Q., Guo, Z., 2020. A review on prevention of sticking during fluidized bed reduction of fine iron ore. *ISIJ Int.* 60 (1), 1–17.
- Guo, Z., Bi, D., Ma, Y., Sun, Z., 2020. Approaches to high-grade sintered magnesia from natural magnesite. *China's Refract.* 29 (3), 7–12.
- Guo, Z., Bi, D., Sun, S., 2021. Manufacturing Principles of Refractory Magnesia in China, *Refractories Worldforum: Manufacturing & Performance of High-Temperature Materials*, pp. 34–41.
- Han, Z., Geng, S., Zeng, X., Xu, S., An, P., Cheng, J., Yang, J., Li, F., Zhang, S., Liu, M., Guan, G., Xu, G., 2018. Reaction decoupling in thermochemical fuel conversion and technical progress based on decoupling using fluidized bed. *Carbon Resour. Convers.* 1 (2), 109–125.
- Han, Z., Zeng, X., Yao, C., Wang, Y., Xu, G., 2016. Comparison of direct combustion in a circulating fluidized bed system and decoupling combustion in a dual fluidized bed system for distilled spirit lees. *Energy Fuel* 30 (3), 1693–1700.
- Hara, M., Kurumada, N., Hashimoto, I., Watanabe, T., 1998. Development of Fluidized Bed Cement Kiln System by Scale-Up Plant. 8th Conference on Coal Utilization Technology, pp. 239–253.
- Hasanbeigi, A., Arens, M., Price, L., 2014. Alternative emerging ironmaking technologies for energy-efficiency and carbon dioxide emissions reduction: a technical review. *Renew. Sustain. Energy Rev.* 33, 645–658.
- He, J., Song, W., Gao, S., Dong, L., Barz, M., Li, J., Lin, W., 2006. Experimental study of the reduction mechanisms of NO emission in decoupling combustion of coal. *Fuel Process. Technol.* 87 (9), 803–810.
- He, M., Sun, Y., Han, B., 2013. Green carbon science: scientific basis for integrating carbon resource processing, utilization, and recycling. *Angew. Chem. Int. Ed.* 52 (37), 9620–9633.
- Hepburn, C., Adlen, E., Beddington, J., Carter, E.A., Fuss, S., Dowell, N.M., Minx, J.C., Smith, P., Williams, C.K., 2019. The technological and economic prospects for CO₂ utilization and removal. *Nature* 575 (7781), 87–97.
- Hinweis, W., 2022. Robert Habeck wants to fill gas storage quickly and relies on coal. <https://newsingermany.com/robert-habeck-wants-to-fill-gas-storage-quickly-and-relies-on-coal/>. (Accessed 14 April 2023).
- IEA (International Energy Agency), 2022. Global energy review: CO₂ emissions in 2021. <https://www.iea.org/reports/global-energy-review-co2-emissions-in-2021-2>. (Accessed 14 April 2023).
- Ishii, H., Hayashi, T., Tada, H., Yokohama, K., Takashima, R., Hayashi, J.-i., 2019. Critical assessment of oxy-fuel integrated coal gasification combined cycles. *Appl. Energy* 233–234, 156–169.

- Jin, Y., Hu, S.Y., Zhang, Z.Y., Zhu, B., Bai, D.R., 2022. The path to carbon neutrality in China: a paradigm shift in fossil resource utilization. *Resour. Chem. Mater.* 1 (1), 129–135.
- Kaminsky, W., 2021. Chemical recycling of plastics by fluidized bed pyrolysis. *Fuel Commun.* 8, 100023.
- Karvonen, J., Kunttu, J., Suominen, T., Kangas, J., Leskinen, P., Judl, J., 2018. Integrating fast pyrolysis reactor with combined heat and power plant improves environmental and energy efficiency in bio-oil production. *J. Clean. Prod.* 183, 143–152.
- Keeling, J., Horn, R., Wilson, I., 2019. New kiln technology expands market opportunities for cryptocrystalline magnesite. *MESA J.* 89 (1), 22–38.
- Khanmohammadi, S., Saadat-Targhi, M., Ahmed, F.W., Afrand, M., 2020. Potential of thermoelectric waste heat recovery in a combined geothermal, fuel cell and organic Rankine flash cycle (thermodynamic and economic evaluation). *Int. J. Hydrogen Energy* 45 (11), 6934–6948.
- Kunwar, B., Cheng, H.N., Chandrashekar, S.R., Sharma, B.K., 2016. Plastics to fuel: a review. *Renew. Sustain. Energy Rev.* 54, 421–428.
- Kvande, H., Drablos, P.A., 2014. The aluminum smelting process and innovative alternative technologies. *J. Occup. Environ. Med.* 56 (5), 23–32.
- Lai, D., Chen, Z., Shi, Y., Lin, L., Zhan, J., Gao, S., Xu, G., 2015. Pyrolysis of oil shale by solid heat carrier in an innovative moving bed with internals. *Fuel* 159, 943–951.
- Li, G., Liu, Q., Liu, Z., 2012. CaC₂ production from pulverized coke and CaO at low temperatures—influence of minerals in coal-derived coke. *Ind. Eng. Chem. Res.* 51 (33), 10748–10754.
- Li, G., Liu, Q., Liu, Z., Zhang, Z.C., Li, C., Wu, W., 2010. Production of calcium carbide from fine biochars. *Angew. Chem. Int. Ed. Engl.* 49 (45), 8480–8483.
- Li, J.-J., Zhang, M., Yang, H.-R., Lu, J.-F., Zhao, X.-X., Zhang, J.-C., 2016. The theory and practice of NO emission control for circulating fluidized bed boilers based on the re-specification of the fluidization state. *Fuel Process. Technol.* 150, 88–93.
- Li, J., Xu, G., Yang, L., Guo, M., Zhang, J., Guo, Y., 1995. A Smokeless Coal Burning Method for Inhibiting the Production of Nitrogen Oxides and a Coal Burning Furnace and its Application. Chinese Patent ZL1110776.
- Li, N., Liu, H., Cheng, Z., Yan, B., Chen, G., Wang, S., 2022. Conversion of plastic waste into fuels: a critical review. *J. Hazard Mater.* 424, 127460.
- Liang, B., Bai, H., Bai, D., Liu, X., 2022. Emissions of non-methane hydrocarbons and typical volatile organic compounds from various grate-firing coal furnaces. *Atmos. Pollut. Res.* 13 (4), 101380.
- Liang, B., Bai, H., Feng, Q., Song, H., Lan, T., Liu, X., 2019. Emissions of particulate matter and polycyclic aromatic hydrocarbons from household coal combustions. *CIESC J.* 70 (8), 2888–2897. <https://doi.org/10.11949/j.issn.0438-1157.20181204>. +3212 (in Chinese).
- Liang, B., Song, H., Bai, H., Wu, Q., Bai, J., Yang, X., Lan, T., 2017. Prevention and control of air pollution from household coal combustions, Part I: a comparative experimental on combustion characteristics of household coal stoves of different designs. *Clean Coal Technol.* 23 (4), 89–94. <https://doi.org/10.13226/j.issn.1006-6772.2017.04.014> (in Chinese).
- Lin, B., Xu, L., 2015. Energy conservation of electrolytic aluminum industry in China. *Renew. Sustain. Energy Rev.* 43, 676–686.
- Lin, L., Zhang, C., Li, H., Lai, D., Xu, G., 2015. Pyrolysis in indirectly heated fixed bed with internals: the first application to oil shale. *Fuel Process. Technol.* 138, 147–155.
- Liu, X., Han, J., Zhang, N., Wang, J., 2019. Status of decentralized civil heating technology in China. *Bull. Chin. Acad. Sci.* 34 (4), 401–408. <https://doi.org/10.16418/j.issn.1000-3045.2019.04.004> (in Chinese).
- Liu, X., Han, Z., Han, J., Liang, B., Zhang, N., Hu, S., Bai, D., Xu, G., 2022. Principle and technology of low-NO_x decoupling combustion based on restructuring reactions. *CIESC J.* 73 (8), 3355–3368. <https://doi.org/10.11949/0438-1157.20220716> (in Chinese).
- Long, X., Spiegl, N., Berruoco, C., Paterson, N., Millan, M., 2020. Fluidised bed oxy-fuel gasification of coal: interactions between volatiles and char at varying pressures and fuel feed rates. *Chem. Eng. Sci.* 8, 100068.
- Lux, S., Baldauf-Sommerbauer, G., Ottitsch, B., Loder, A., Siebenhofer, M., 2019. Iron carbonate beneficiation through reductive calcination—parameter optimization to maximize methane formation. *Eur. J. Inorg. Chem.* 2019 (13), 1748–1758.
- Lux, S., Baldauf-Sommerbauer, G., Siebenhofer, M., 2018. Hydrogenation of inorganic metal carbonates: a review on its potential for carbon dioxide utilization and emission reduction. *ChemSusChem* 11 (19), 3357–3375.
- Maurits, J.E.A., 2014. Chapter 2.6 silicon production. In: Seshadri, S., Alexander, M., Roderick, G., Seetharaman, S. (Eds.), *Treatise on Process Metallurgy*. Elsevier, pp. 919–948.
- MercoPress, 2022. German “Green” minister admits electricity coal burning plants will have to go back into production. <https://en.mercoPress.com/2022/06/21/german-green-minister-admits-electricity-coal-burning-plants-will-have-to-go-back-into-production>. (Accessed 14 April 2023).
- Mi, Y., Zheng, D., Guo, J., Chen, X., Jin, P., 2014. Assessment of energy use and carbon footprint for low-rank coal-based oxygen-thermal and electro-thermal calcium carbide manufacturing processes. *Fuel Process. Technol.* 119, 305–315.
- Mikulčić, H., Klemenč, J.J., Vujanović, M., Urbanec, K., Duić, N., 2016. Reducing greenhouse gases emissions by fostering the deployment of alternative raw materials and energy sources in the cleaner cement manufacturing process. *J. Clean. Prod.* 136, 119–132.
- Miller, B.G., 2017. Carbon dioxide emissions reduction and storage. In: Miller, B.G. (Ed.), *Clean Coal Engineering Technology*, second ed. Elsevier, Boston, pp. 609–668.
- Mom, A.J.A., 2013. Introduction to gas turbines. *Mod. Gas Turbine Syst.* 3–20.
- Mousa, E., Wang, C., Riesbeck, J., Larsson, M., 2016. Biomass applications in iron and steel industry: an overview of challenges and opportunities. *Renew. Sustain. Energy Rev.* 65, 1247–1266.
- NBS (National Bureau of Statistics of China), 2022. China Statistical Yearbook 2022. Chinese Statistics Press, Beijing.
- Nie, S., Zhou, J., Yang, F., Lan, M., Li, J., Zhang, Z., Chen, Z., Xu, M., Li, H., Sanjayan, J. G., 2022. Analysis of theoretical carbon dioxide emissions from cement production: Methodology and application. *J. Clean. Prod.* 334, 130270.
- Oki, Y., Hamada, H., Kobayashi, M., Yuri, I., Hara, S., 2017. Development of high-efficiency oxy-fuel IGCC system. *Energy Proc.* 114, 501–504.
- Oki, Y., Inumaru, J., Hara, S., Kobayashi, M., Watanabe, H., Umemoto, S., Makino, H., 2011. Development of oxy-fuel IGCC system with CO₂ recirculation for CO₂ capture. *Energy Proc.* 4, 1066–1073.
- Pourkazie, S.M., Ahmadi, M.H., Sadeghzadeh, M., Moosavi, S., Pourfayaz, F., Chen, L., Pour Yazdi, M.A., Kumar, R., 2019. Thermoelectric cooler and thermoelectric generator devices: a review of present and potential applications, modeling and materials. *Energy* 186, 115849.
- Ronsse, F., Nachenius, R.W., Prins, W., 2015. Chapter 11-Carbonization of biomass. In: Pandey, A., Bhaskar, T., Stöcker, M., Sukumaran, R.K. (Eds.), *Recent Advances in Thermo-Chemical Conversion of Biomass*. Elsevier, Boston, pp. 293–324.
- Sandvig, E., Walling, G., Brown, R.C., Pletka, R., Radlein, D., Johnson, W., 2003. Integrated Pyrolysis Combined Cycle Biomass Power System Concept Definition Final Report. Alliant Energy, Iowa State University, DynaMotive Energy Systems Corp, Black & Veatch Corporation. Report No. DE-FS26-01NT41353. <https://www.osti.gov/biblio/826269>.
- Schenk, J.L., 2011. Recent status of fluidized bed technologies for producing iron input materials for steelmaking. *Particuology* 9 (1), 14–23.
- Shahin, H., Hassanpour, S., Saboonchi, A., 2016. Thermal energy analysis of a lime production process: rotary kiln, preheater and cooler. *Energy Convers. Manag.* 114, 110–121.
- Shan, Y., Guan, D., Zheng, H., Ou, J., Li, Y., Meng, J., Mi, Z., Liu, Z., Zhang, Q., 2018. China CO₂ emission accounts 1997–2015. *Sci. Data* 5, 170201.
- Shan, Y., Huang, Q., Guan, D., Hubacek, K., 2020. China CO₂ emission accounts 2016–2017. *Sci. Data* 7 (1), 54.
- Shan, Y., Liu, Z., Guan, D., 2016. CO₂ emissions from China’s lime industry. *Appl. Energy* 166, 245–252.
- Shan, Y., Zhou, Y., Meng, J., Mi, Z., Liu, J., Guan, D., 2019. Peak cement-related CO₂ emissions and the changes in drivers in China. *J. Ind. Ecol.* 23 (4), 959–971.
- Spiegl, N., Berruoco, C., Long, X., Paterson, N., Millan, M., 2020. Production of a fuel gas by fluidised bed coal gasification compatible with CO₂ capture. *Fuel* 259, 116242.
- Spiegl, N., Long, X., Berruoco, C., Paterson, N., Millan, M., 2021. Oxy-fuel co-gasification of coal and biomass for negative CO₂ emissions. *Fuel* 306, 121671.
- Spreitzer, D., Schenk, J., 2019. Reduction of iron oxides with hydrogen—a review. *Steel Res. Int.* 90 (10), 1900108.
- Steckel, J.-C., Jakob, M., 2022. To end coal, adapt to regional realities. *Nature* 607, 29–31.
- Sun, C., Yan, B., Cai, C., Han, Z., Xu, G., 2020. Characteristics of reaction and product microstructure during light calcination of magnesite in transport bed. *CIESC J.* 71, 5735–5744. <https://doi.org/10.11949/0438-1157.20200530> (in Chinese).
- Tan, G., Ohta, M., Kanatzidis, M.G., 2019. Thermoelectric power generation: from new materials to devices. *Phil. Trans.* 377, 20180450.
- Thunman, H., Berdugo Vilches, T., Seemann, M., Maric, J., Vela, I.C., Pissot, S., Nguyen, H.N.T., 2019. Circular use of plastics—transformation of existing petrochemical clusters into thermochemical recycling plants with 100% plastics recovery. *Sustain. Mater. Technol.* 22, e00124.
- Vehec, J.R., 2010. Technology Roadmap Research Program for the Steel Industry. American Iron and Steel Institute, Washington.
- Wang, J., Liu, X.C., Xia, S.Q., Tao, X.T., 2013. Ca(1-x)RE(x)Ag(1-y)Sb (RE = La, Ce, Pr, Nd, Sm; 0 < x < 1; 0 < y < 1): interesting structural transformation and enhanced high-temperature thermoelectric performance. *J. Am. Chem. Soc.* 135 (32), 11840–11848.
- Wang, Q., Wang, W., Liu, M., Lyu, J., Liu, J., Yue, G., 2021. Development and the prospect of (ultra) supercritical coal-fired power generation technology. *Therm. Power Gener.* 50 (2), 1–9. <https://doi.org/10.19666/j.rld.202007179> (in Chinese).
- Wang, R., Ji, L., Liu, Q., Zheng, D., Liu, H., Liu, Z., 2014. Development of auto-thermal production of calcium carbide. *CIESC J.* 65 (7), 2417–2425. <https://doi.org/10.3969/j.issn.0438-1157.2014.07.003> (in Chinese).
- Wang, X., Xu, L., 2022. Current situation and trend analysis of carbon emission in the electrolytic aluminum industry. *Energy Sav. Nonferrous Metal.* 38 (4), 1–6. <https://doi.org/10.19610/j.cnki.cn11-4011/xf.2022.04.001> (in Chinese).
- Wu, L., Guene Loughou, B., Jiang, B., Zhang, H., Guo, Y., Geng, B., Yan, T., Lapka, P., Shuai, Y., 2023. Experimentally validated numerical model of multi-spectral bands radiative transport in solar receiver/reactor with photo-active porous absorber reacting media. *Energy Convers. Manag.* 278, 116740.
- Xakalashie, B.S., Tangstad, M., 2011. Silicon processing - from quartz to crystalline silicon solar cells. In: Jones, R.T., den Hoed, P. (Eds.), *Southern African Pyrometallurgy*. Southern African Institute of Mining and Metallurgy, Johannesburg, pp. 83–99.
- Xu, G., 2019. Preface of special issue for engineering thermochemistry. *CIESC J.* 70 (8), 2821–2822 (in Chinese). <https://hgxb.cip.com.cn/CN/Y2019/V70/I8/0> (in Chinese).
- Xu, G., Bai, D., Xu, C., He, M., 2022. Challenges and opportunities for engineering thermochemistry in carbon-neutralization technologies. *Natl. Sci. Rev.* Nwac217.
- Xu, W., Wang, H., Cui, X., Zhang, Z., 2021. Research progress on cleaner production and engineering of calcium carbide preparation. *Chem. Ind. Eng. Prog.* 40 (10), 5337–5347. <https://doi.org/10.16085/j.issn.1000-6613.2020-2156> (in Chinese).
- Yao, C., Dong, L., Wang, Y., Yu, J., Li, Q., Xu, G., Gao, S., Yi, B., Yang, J., 2011. Fluidized bed pyrolysis of distilled spirits lees for adapting to its circulating fluidized bed decoupling combustion. *Fuel Process. Technol.* 92 (12), 2312–2319.

- Yue, G., Cai, R., Lu, J., Zhang, H., 2017. From a CFB reactor to a CFB boiler-The review of R&D progress of CFB coal combustion technology in China. *Powder Technol.* 316, 18–28.
- Yue, G., Zhou, D., Tian, W., Ma, L., Liu, Q., Chong, C., Wang, Z., Long, H., Liao, H., 2018. Preliminary discussion on the technology roadmap of clean coal combustion in China. *Chin. J. Eng. Sci.* 20 (3), 74–79. <https://doi.org/10.15302/J-SSCAE-2018.03.011> (in Chinese).
- Yuko, T., Ikabata, T., Akiyama, T., Yamamoto, T., Kurumada, N., 2000. New clinker formation process by the fluidized bed kiln system. *Cement Concr. Res.* 30, 1113–1120.
- Zhang, C., Wu, R., Xu, G., 2014. Coal pyrolysis for high-quality tar in a fixed-bed pyrolyzer enhanced with internals. *Energy Fuel.* 28, 236–244.
- Zhang, H., Sun, W., Li, W., Ma, G., 2022. A carbon flow tracing and carbon accounting method for exploring CO₂ emissions of the iron and steel industry: an integrated material–energy–carbon hub. *Appl. Energy* 309, 118485.
- Zhang, J., Wu, R., Zhang, G., Yu, J., Yao, C., Wang, Y., Gao, S., Xu, G., 2013. Technical review on thermochemical conversion based on decoupling for solid carbonaceous fuels. *Energy Fuel.* 27 (4), 1951–1966.
- Zhang, Q., Yi, H., Yu, Z., Gao, J., Wang, X., Lin, H., Shen, B., 2018. Energy-exergy analysis and energy efficiency improvement of coal-fired industrial boilers based on thermal test data. *Appl. Therm. Eng.* 144, 614–627.
- Zhao, H., Tian, X., Ma, J., Chen, X., Su, M., Zheng, C., Wang, Y., 2020. Chemical looping combustion of coal in China: comprehensive progress, remaining challenges, and potential opportunities. *Energy Fuel.* 34 (6), 6696–6734.
- Zhao, L., Feng, J., Dong, H., 2022. Analysis of carbon footprint and reduction approach of magnesia production in China. *J. Clean. Prod.* 334, 130194.
- Zhao, R., Min, N., Geng, Y., He, Y., 2017. Allocation of carbon emissions among industries/sectors: an emissions intensity reduction constrained approach. *J. Clean. Prod.* 142, 3083–3094.
- Zheng, L., 2011. Overview of oxy-fuel combustion technology for carbon dioxide (CO₂) capture. In: Zheng, L. (Ed.), *Oxy-fuel Combustion for Power Generation and Carbon Dioxide (CO₂) Capture*. Woodhead Publishing, pp. 1–13.
- Zhou, S., Chen, Z., Ma, W., Li, S., Yang, X., Cao, S., 2021. Effects of grinding media on the material properties and strengthening mechanism of silicon production. *J. Clean. Prod.* 278, 123438.
- Zhou, Y., Zhou, H., Xu, C., 2022. Exploration of hydrogen sources for the low-carbon and green production in the steel industry in China. *Chem. Ind. Eng. Prog.* 41 (2), 1073–1077. <https://doi.org/10.16085/j.issn.1000-6613.2022-0005> (in Chinese).