

Electrolysers for producing net-zero heat

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In addition to fuel cell applications, water electrolysis affords several opportunities for producing high-grade heat by utilising electrolytic hydrogen and oxygen in combustion applications. This can reduce or eliminate the atmospheric emissions associated with the combustion of conventional fuels. Importantly, net-zero heat can be produced if the electrolyser is powered by renewable electricity, whereby the output gases may be termed green hydrogen and green oxygen. This paper provides an overview of prospective applications for electrolysers in the heat sector by considering three general implementation pathways based on how the electrolytic oxygen is used.

Introduction

The combustion of hydrocarbon fuels to produce heat results in several atmospheric emissions that are damaging to human health and the environment. To date, most efforts to address this global problem have been focused on implementing end-of-pipe clean-up solutions, which incur energy and cost penalties (e.g. catalytic converters, particulate filters, CO₂ capture and sequestration/CCS). The alternative approach for minimising emissions involves switching fuels, from hydrocarbons to green hydrogen. Green hydrogen can be used to completely replace a hydrocarbon fuel, or to reduce its emissions by blending/co-firing. However, the combustion of hydrogen in air results in NO_x emissions. Therefore a source of oxygen other than air is required if NO_x emissions are to be eradicated.

Electrolytic oxygen can be used as the oxidant, while electrolytic hydrogen is either combusted or dedicated to a separate end use. By definition, water electrolysis produces high-purity hydrogen and oxygen simultaneously in stoichiometric ratio (i.e. in the correct quantities to enable complete combustion and so maximise the flame temperature and rate of heat release). Provided that the electrolyser is supplied with renewable electricity, there are no harmful atmospheric emissions, upstream or downstream. The only emission is water vapour, which replenishes the water consumed by the electrolysis process.^[1]

The co-production of hydrogen and oxygen by an electrolyser affords three general implementation pathways in the heat sector, based on how the electrolytic oxygen is used. The first, or default, approach is to vent oxygen to atmosphere at the point of production. This

acts to counterbalance the consumption of atmospheric oxygen at the points of hydrogen use and so helps to ameliorate the global problem of oxygen depletion.^[1] By liberating oxygen, electrolysis delivers an environmental benefit relative to other fuel production processes; arguably this should be attributed a financial value, especially if green oxygen is being released. In practice this first pathway involves, for example, deploying Power-to-Gas systems for injecting hydrogen admixtures into natural gas distribution networks,^[2, 3] or injecting hydrogen into future hydrogen transmission networks.^[4]

The second pathway is to inject electrolytic oxygen into the air intake of a combustion process, or directly into the heating zone by using 'oxy-fuel' burners and oxygen lances.^[5] The use of oxygen by furnaces and kilns is a long established approach for improving thermal performance and reducing emissions. The use of electrolytic oxygen in these existing market applications will improve the economics of hydrogen production, irrespective of the hydrogen application.

The third pathway is to use both gases simultaneously to produce a hydrogen-oxygen flame, or steam, for a relevant thermal process. The electrolyser's function is to enable hydrogen to be oxidised to produce heat without consuming air. This approach provides a truly zero-emission solution.

The first pathway has been discussed previously,^[1–3] so this paper focuses mainly on the second and third pathways. Economic analyses of switching from hydrocarbon fuels to electrolytic hydrogen, or to using electrolytic oxygen in certain thermal processes, are beyond the scope of this paper. Clearly, in the context of decarbonisation and pollution abatement, prospective electrolyser applications in the

heat sector need to be compared with direct electrification options where they exist, and preferred solutions identified.

Combustion properties

The use of oxygen to enhance combustion was demonstrated by Lavoisier in 1782 by successfully melting platinum for the first time (melting point = 1768°C). Oxygen was then exploited in the Bude-Light patented by Gurney in 1839, a variation of which was used to illuminate the House of Commons for over 50 years.^[6] The invention of a hydrogen-oxygen flame torch or blowpipe is attributed to Hare and Clarke in the early 1800s.^[7] These were used before coal gas or cylinders of acetylene and propane became widely distributed. Hydrogen and oxygen have since been used in several industrial settings, but rarely together due to the comparatively low cost of combusting fossil fuels in (free) air.

Hydrogen and oxygen offer different value propositions for enhancing industrial thermal processes. For example, hydrogen may be used as a reducing atmosphere for annealing steel alloys, and oxygen as a means for increasing flame temperatures. When compared with other fuels, electrolytic hydrogen is characterised by a remarkably distinct set of properties, including a very high purity, a very low ignition energy requirement, wide flammability and detonation limits, a high flame speed, no soot or particulate emissions, and a very low flame emissivity [see [Table 1](#)]. If combusted in air, the wide flammability limits of hydrogen permit NO_x emissions to be reduced by operating at lean equivalence ratios (i.e. with excess air), although this reduces flame temperatures. Alternatively, the combustion of hydrogen in oxygen will achieve a much higher flame temperature, a more visible flame and no NO_x emissions. Also, a hydrogen-oxygen flame is the easiest to model mathematically, because it can be described with fewer species and elementary reactions than the simplest hydrocarbon fuel (methane).^[8]

Property	Value	Comment
Higher heating value	142 MJ/kg 12 MJ/m ³	2.5–15 times the MJ/kg of conventional fuels 23–70% of the MJ/m ³ of conventional fuels
Density	0.09 kg/m ³	Approximately one-seventh that of natural gas
Ignition energy requirement	0.0012 mJ H ₂ -O ₂ 0.019 mJ H ₂ -air	0.28 mJ methane-air 0.8 mJ petrol-air
Adiabatic flame temperature	~2800°C H ₂ -O ₂ ~2200°C H ₂ -air	~2800°C for propane-oxygen ~3150°C for acetylene-oxygen
Flame speed	~2 m/s H ₂ -O ₂ (stoichiometric conditions)	~0.37 m/s for methane-air
Flammability limits	4–94% H ₂ -O ₂ 4–74% H ₂ -air	1.4–7.6% for petrol in air 2.5–81% for acetylene in air 4.0–16% for methane in air
Detonation limits	15–90% H ₂ -O ₂ 18–59% H ₂ -air	2.8–4.5% petrol in air 4.2–50% for acetylene in air 5.7–14% methane in air
Flame emissivity	~0.03 H ₂ -air	>0.95 for coal in air ~0.8 for diesel in air 0.3–0.6 for methane in air
Research octane number (RON)	~140	95 for premium unleaded petrol
Auto ignition temperature	~580°C in air	~230°C for petrol ~305°C for acetylene

Table 1. Combustion properties of hydrogen.

Careful engineering design to achieve failsafe operation is essential for combustion systems utilising electrolytic hydrogen and oxygen, because of their respective properties. There is a fundamental need to seclude hydrogen, because a very small electrostatic spark discharge from an isolated conductor (e.g. a person) is sufficient to ignite a hydrogen leak, which may result in a fire or detonation.^[9] Also, when used in place of air, electrolytic oxygen adds substantially to safety concerns because of its high reactivity. An oxygen leak which raises the local concentration in air only slightly (e.g. from 20.9% to 24%) is sufficient to create a dangerous situation, and any material will become a fuel in an oxygen fire.^[10] In general, it is preferable for the electrolyser to operate at low pressure (<0.5 bar), because high-pressure oxygen can react violently with common materials and cause spontaneous combustion. Importantly, one of the major advantages of using an electrolyser for heat generation is that terminating the power supply will terminate oxygen and hydrogen production, which substantially reduces the hazard for operators and first-responders in a fire situation (whatever the cause), especially when compared with the existing industrial practice of using compressed gas cylinders.

Co-firing and combusting hydrogen blends

Electrolytic hydrogen can be used to reduce the greenhouse gas (GHG) footprint of an existing thermal process by partially displacing a fossil fuel, while electrolytic oxygen is vented to atmosphere. A blend of hydrogen and natural gas can be injected into the gas supply prior to combustion, or hydrogen may be combusted separately alongside the conventional fuel. Generally at low hydrogen concentrations (e.g. 5% by volume), the combustion of a blend has little effect on flame characteristics and heat transfer rates, but as the concentration increases the blend's calorific value declines and its propensity to flashback increases (i.e. a small explosion that occurs in a burner when the gas flow rate is reduced to zero). Accordingly, it has been recommended that the hydrogen concentration used by existing domestic appliances is limited to 30%,^[11] which equates to achieving a GHG saving of approximately 10%. Realising greater savings by adopting higher concentrations requires burners to be modified or appliances to be replaced. Similarly, engines can be designed and controlled to operate on various blend

concentrations. However, for achieving the overarching net zero objective, it is generally considered that all gas-fired equipment will need to transition to 100% hydrogen or be substituted with equivalent electrical equipment.

Utilising electrolytic oxygen

Electrolytic oxygen can be used as a performance enhancer for industrial thermal processes. These generally employ temperatures of up to about 1350°C for processing common metals (e.g. melting, forging, annealing, tempering) and up to 1650°C for processing non-metals (e.g. kiln firing, glass and cement production). This is conventionally achieved by hydrocarbon flames, for instance in steel furnaces where heat is transferred to the stock primarily by thermal radiation. Enriching air with oxygen increases the flame temperature, while reducing flue gas heat losses because less air needs to be consumed per MWh of heat production. This reduces heating times, improves product quality and, at high levels of oxygen enrichment, substantially reduces NO_x and particulate emissions.^[5, 12] However, the flame temperature increases at a declining rate with oxygen concentration, because dissociation reactions among the combustion products absorb an increasing amount of energy (to form carbon monoxide, hydrogen and various free radicals and atoms). Fortunately, modest increases in oxygen concentration are beneficial, because relatively small increases in flame temperature (e.g. by 50–150°C) can achieve significant improvements in radiative heat transfer due to the Stefan-Boltzmann law.^[13]

Oxygen enrichment is employed in furnaces up to concentrations of about 35%, although if the burners are not replaced this is usually limited to about 25%. For processes co-firing biomass with a fossil fuel, a higher proportion of biomass can be used if the flame temperature is increased by adding oxygen (and hence greater GHG savings achieved). Similarly for kilns, oxygen enrichment can enable a greater throughput by virtue of increasing the operating temperature (e.g. it has been reported that the temperature of a natural gas-fired kiln can be increased from 1570°C to approximately 2000°C by increasing the oxygen concentration to 30%^[14]).

Alternatively, oxygen may be injected directly beneath an existing flame so that the hottest region of the flame is facing the stock. This is particularly beneficial in metal and glass melting processes and in rotary kilns, because it increases radiation to the stock without significantly affecting heat transfer to the furnace roof, so helping to improve thermal

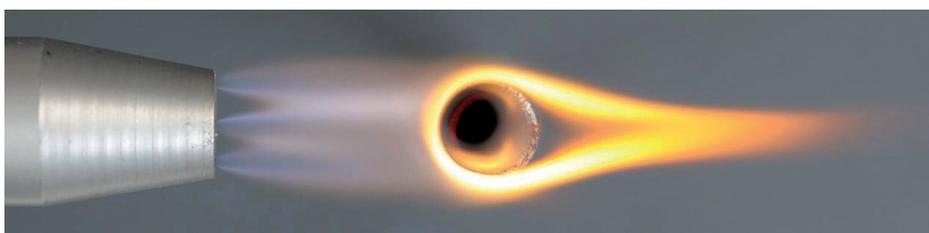


Figure 1. A surface-mix burner being used to braze a copper pipe joint by combusting electrolytic hydrogen and oxygen in stoichiometric quantities.

efficiency while preserving the life of the refractory. Large reductions in emissions can also be achieved by using lances and oxy-fuel burners to supplement or replace conventional burners. For glass melting furnaces, savings of 70–90% in NO_x emissions, 20–70% in particulates and 50% in specific energy consumption (and hence GHG emissions) have been reported as a result of using multistage oxy-fuel burners.^[15] Also if a process such as cement production is designed to use only oxy-fuel burners, the CO₂ concentration in the flue gas can reach 85%, which improves the viability of implementing CCS.^[16, 17]

Blowing oxygen through a lance over molten pig iron to reduce its carbon content and convert it into steel is an exothermic process, which has been known since Bessemer patented basic oxygen steelmaking in 1856. Oxygen may also be applied to reduce the electricity consumption of an electric arc furnace that processes steel scrap and direct reduced iron (DRI); oxygen lances can be used to cut the scrap, to increase the rate at which it is heated, and to inject oxygen at supersonic velocities into the molten steel in order to refine it.^[18] In addition, electrolytic hydrogen can be used in both types of furnace as the chemical reducing agent for removing oxygen from iron ore (i.e. to produce the DRI for an arc furnace and to displace coal/coke in a blast furnace). Importantly, the application of this approach to arc furnaces can fully decarbonise steel production.^[19–21]

Oxygen use is currently framed by the available scale of liquid oxygen deliveries or pressure swing adsorption (PSA) units. The latter typically produce oxygen at rates of up to about 100 tonnes/day, which equates to the oxygen produced by a 30 MW electrolyser operating continuously. For comparison, if hydrogen is used as a reducing agent in a blast furnace producing 12 000 tonnes/day of hot metal, an electrolyser of about 750 MW operating continuously would be needed (assuming a requirement of 27.5 kgH₂ per tonne of hot metal^[22]). Processes such as steel, glass and cement production are therefore well suited to utilising both electrolytic oxygen and hydrogen, and to using oxygen to a greater extent than conventionally practised.

Hydrogen-oxygen flames

A hydrogen-oxygen flame impinging on a solid surface or joint is a very effective way of heating the desired area rapidly. When compared with a hydrogen-air flame, the lack of nitrogen flowing through the burner increases the maximum flame temperature by about 600°C and eliminates NO_x emissions, while the flame itself is slightly more visible to the naked eye. The flame temperature is broadly similar to that achieved when combusting propane-oxygen or oxy-acetylene, but it is characterised by a very low flame emissivity (luminosity) due to the absence of carbon in the fuel.^[23] Therefore hydrogen-oxygen combustion preferably requires the flame to impinge directly onto the surface that is being heated, or onto a suitable intermediate surface for re-radiating heat. Accordingly, because flame radiation is a major design consideration for high-temperature processes, switching from hydrocarbon fuels to hydrogen is not necessarily a straightforward option.

The two gas streams emerging from an electrolyser can be easily and safely ignited by means of a burner that is designed to combust the stoichiometric production rates of hydrogen and oxygen. It is desirable to employ post-mixed or ‘surface-mix’ combustion where each gas arrives separately at the surface of the burner, rather than pre-mixed combustion, because this avoids the hazard presented by having a hydrogen-oxygen mixture within the burner itself, and allows a quiet stable and relatively homogeneous laminar flame to be produced.^[24] The high diffusivity and high flame speed of hydrogen require the burner orifices to be designed to ensure the downstream flow behaviour of each gas prevents the resulting flame from entering the mouth of the burner. The burner remains relatively cool during use, because no combustible mixture exists upstream of the burner surface. Heat is transferred mainly by convective impingement, and so a flame can be used to lap around a surface or joint, while radiative losses remain relatively low [see [Figure 1](#)].

For processes requiring variable heating rates, an excellent level of flame control and heat input

can be achieved electrically. The heat flux and flame length can be adjusted by regulating the power input to the electrolyser stack (rather than by adjusting the flow rates of the two gases) and the flame can always be reproduced precisely. At any power level the burner will issue sufficient electrolytic oxygen to completely combust the co-produced hydrogen, but if a reducing flame is required, a bypass route can be employed to divert some of the oxygen to atmosphere. When produced by a proton-exchange membrane (PEM) electrolyser, the electrolyser/burner system is relatively compact and lightweight, and the heating rate can be adjusted on a sub-second basis. These are significant advantages both for manual and automated flame processes. There are also practical and safety benefits for the operator when undertaking joining processes (e.g. brazing), because there is no need to handle heavy pressurised cylinders of hydrocarbon fuels and oxygen.

For open flame processes this approach may be applied at the 1–100 kWt scale with a portable electrolyser, which is simply connected to an available mains electricity supply close to the point of use, or at a larger scale by means of a stationary electrolyser located within an industrial plant. If the heating process occurs at a fixed location and a flue is employed, both water and latent heat can be recovered from the exhaust. Finally, in manufacturing settings, high-power flames are often required intermittently for relatively short durations at multiple locations, so attention needs to be given to the associated impact of coincident power demands on the factory’s overall electricity demand profile.

Steam generators

Steam is used for a wide range of purposes (e.g. by the food processing and paper industries, in pellet mills and oil refineries, for power generation, process heating, atomising heavy fuels, humidifying air, cleaning/sterilising surfaces, and heating large buildings). When electrolytic hydrogen and oxygen are combined, the combustion product is superheated sterile steam. The ability to provide energy in the form of steam, rather than a flame, considerably extends the applications and benefits of the third pathway. For example, steam is an efficient and well proven means for transferring heat across industrial sites and heat networks; for dissipating heat in a uniform manner without overheating or polluting the item being heated; and for generating electricity via steam turbines.

The output gases from an electrolyser can be converted to steam on-demand via a suitable burner and combustion chamber [see [Figure 2](#)].

By injecting an appropriate amount of water into the post-combustion zone, the amount of steam generated by the electrolyser may be increased and its temperature decreased to a desired level. In this way superheated or saturated steam can be readily reproduced for a given application, or the enthalpy adjusted as required prior to being injected immediately into an existing steam-raising process.^[25–28] This is a relatively simple technological solution that is extremely compact, with a power density that is approximately seven orders of magnitude greater than a conventional steam plant.^[25]

This approach has been demonstrated at multi-MW scale, and several potential applications exist at a larger scale in the energy sector (e.g. to increase the peak capacity, efficiency and response of power generators; to provide backup power; to reduce steam turbine startup times; to improve steam quality for geothermal power plants; to act as a gasifying agent for biomass gasifiers; and to provide a boost when needed by district heating networks).^[28–31] There are also several other electrolyser applications that deserve further consideration with respect to sterilising, cleaning, humidifying, drying and propulsion.^[30] In general, a rapid-response PEM electrolyser can be used to satisfy a short-duration requirement for superheated steam on-demand, but in some cases it may be preferable to store both hydrogen and oxygen, so that electrolyser operation and steam generation can occur out of time phase (e.g. with the electrolyser operating during periods of low-price electricity and steam generation occurring during peak demand periods).

Heat engines

Hydrogen has been combusted in engines since the original work of de Rivaz in 1804 and Cecil in 1820.^[32] Later Tsiolkovsky conceived of using hydrogen-oxygen combustion to propel a spacecraft, and in 1903 he proposed a manned rocket fueled by liquid hydrogen and liquid oxygen.^[33] In 1923 Oberth showed that hydrogen-oxygen achieves the greatest jet velocity per unit mass of propellant, and developed the theory that underpinned subsequent rocket development.^[34] Experiments with hydrogen as the fuel for jet engines commenced in 1945, and hydrogen-air engines have since been successfully demonstrated in several applications, including gas turbines (for combusting hydrogen and hydrogen/methane blends) and road vehicles.^[34–39] At present, the principal engine application for hydrogen-oxygen combustion is the rocket engine. For propulsion a rocket uses the mass flow of the expanding steam exiting from a high-pressure combustion chamber (up to 200 bar) to form a

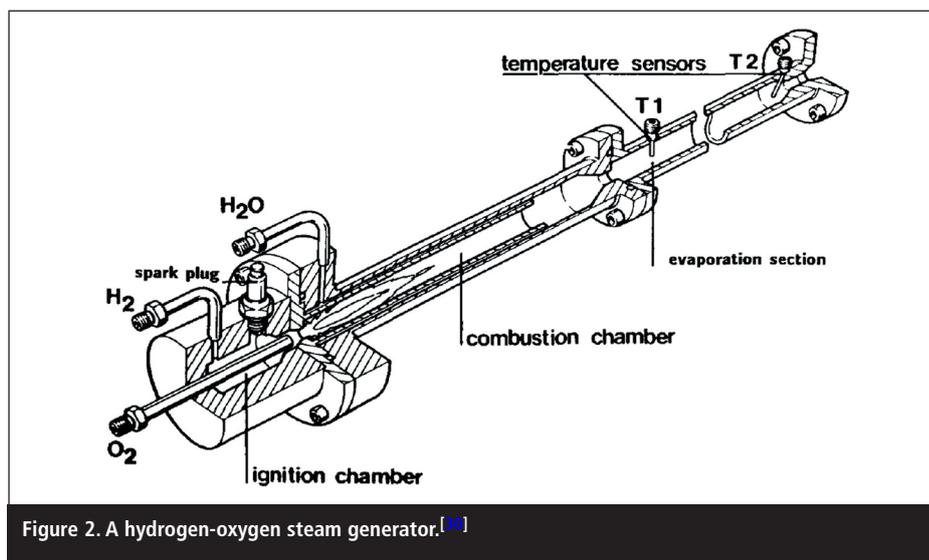


Figure 2. A hydrogen-oxygen steam generator.^[30]

jet with a velocity of at least Mach 10. The most common arrangement is to use liquid hydrogen rather than a hydrocarbon fuel with liquid oxygen, because this permits achieving the greatest specific impulse.^[39]

The very high octane number of hydrogen relative to hydrocarbon fuels allows internal combustion engines to use much higher compression ratios without experiencing knock, and so achieve greater thermal efficiencies. Hydrogen cannot be combusted by compression ignition alone due to its relatively high auto ignition temperature, so to initiate combustion either a spark or some form of pre-chamber jet ignition is required.^[37] The spark ignition energy requirement itself is very low (because the flame speed of hydrogen is several times that of petrol or natural gas), and so hot spots in a combustion chamber can cause premature ignition. The high diffusivity of hydrogen enables rapid mixing with the oxidant and uniform combustion, but its low density restricts the cylinder filling capability and hence the engine's power output. For an air-fed engine, the hydrogen in a stoichiometric mixture can only occupy 29.6% of the combustion chamber volume due to the presence of nitrogen in the fuel/air mixture ($2\text{H}_2 + \text{O}_2 + 3.76\text{N}_2$). Furthermore, it occupies even less of the available volume if the engine is operated at weak equivalence ratios in order to reduce NO_x production. However, hydrogen will occupy 66.7% of the volume of the combustion chamber if oxygen is used rather than air ($2\text{H}_2 + \text{O}_2$). Hence for a given engine capacity, a substantially increased power output can be achieved by using electrolytic oxygen to partially or fully replace air.

From the second law of thermodynamics, the maximum thermal efficiency of an idealised heat engine is governed by the Carnot efficiency ($\zeta = 1 - T_c/T_h$). Accordingly, a

maximum thermal efficiency of about 90% is theoretically achievable for an engine combusting hydrogen-oxygen that rejects heat at ambient temperature, assuming a reversible cycle with adiabatic isothermal processes. A hydrogen-oxygen engine thus offers the potential to achieve both a very high efficiency and zero emissions. For example, thermodynamic cycles have been proposed for achieving power generation efficiencies of over 70%.^[36, 37]

In recent years, to a large extent the focus of engineering development has moved away from developing heat engines to developing renewable power generators for the electricity sector and hydrogen fuel cells for the transport sector. These are zero-emission technologies that can produce electricity without first needing to generate heat. In the case of vehicles, fuel cells permit the use of electric powertrains, which are much more efficient than mechanical powertrains and hence enable a longer range to be achieved for a given amount of onboard hydrogen storage. It should also be noted that the use of electrolytic oxygen in place of air can lead to a significant increase in fuel cell efficiency, including the round-trip efficiency of an energy storage system employing electrolysers and fuel cells.^[40, 41]

Conclusions

Net-zero heat has a new significance given the international imperative to decarbonise. The present widespread production of heat by fossil fuel combustion contravenes this objective, because it treats the Earth's atmosphere as an infinite source of oxygen and an infinite sink for GHGs and pollutant emissions. Conversely, the alternative approach of using water electrolysis to yield both the fuel and the oxidant acts to conserve atmospheric oxygen

and avoid emissions.

Overall, there is considerable potential for electrolyzers to facilitate the production of net-zero heat across a wide range of industrial processes (e.g. in steelmaking, glass production, cement production, power generation, process heating, district heating, and brazing). Electrolyzers can improve both the thermal and environmental performances of combustion processes by substituting electrolytic hydrogen for hydrocarbon fuels and/or electrolytic oxygen for air. By enriching air or completely replacing it, electrolytic oxygen can by itself improve the efficiency of a combustion process. Using both gases together enables a high-temperature flame or steam to be produced without forming NO_x, because no heating of nitrogen takes place. High rates of heat transfer and power generation can thereby be achieved, where the gases are either combusted directly as they emerge from the electrolyser or by using hydrogen and oxygen storage facilities.

As Jules Verne predicted in 1874, ‘water will one day be employed as a fuel, that hydrogen and oxygen that constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable’.^[42]

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Research Trends

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