

煤电碳捕集制合成燃料的全链条技术进展

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摘要: 随着“双碳”目标的提出, 燃煤发电行业必须同时承担减排责任和能源安全责任。利用燃煤电厂集中的二氧化碳排放源, 将碳捕集(CC)与二氧化碳加氢生产合成燃料(e-Fuels)相结合, 可以成为燃煤发电低碳转型的一条可行途径。本文考察了完整的“CC to e-Fuels”技术链, 概述了系统边界和关键耦合环节。文章回顾了逆水煤气变换、费托合成、甲醇衍生化和直接加氢制烃等主流工程与实验室先进技术路线, 并探讨了反应器类型、催化剂体系、原料气特性和工艺集成对系统性能的影响。综述分析表明, “CC to e-Fuels”的关键不仅在于单个装置的效率, 而更多是在于碳捕集、氢气供应和合成转化之间的匹配与协调, 以及在多装置耦合下实现能效与政策经济性的协同考量。总体而言, 在实现减排效益, 可以有效连接源头排放和下游合成, 并满足合理的能源和工程限制的情况下, 该路线就具备大规模示范和工程应用的基础, 并可为燃煤发电的低碳转型提供有价值的补充。

关键词: 碳捕集; 制氢路线; 合成气生成; 合成气转化; 合成燃料认证与经济性

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Full-chain technological advances in e-fuels production from carbon capture in coal-fired power plants

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Abstract: Under the dual-carbon strategy, coal-fired power plants confront increasing pressure to reduce CO₂ emissions while maintaining energy security. Coupling carbon capture (CC) with CO₂ hydrogenation to synthetic fuels (e-Fuels) provides a promising pathway for the low-carbon transition of coal power. This review focuses on the full-chain "CC to e-Fuels" system, covering carbon capture, hydrogen supply, syngas generation, fuel synthesis, and process integration. Major units, including reverse water-gas shift, Fischer - Tropsch synthesis, methanol-derived pathways, and direct CO₂ hydrogenation, are summarized. The analysis shows that the key challenge lies in the coordinated matching of carbon capture, hydrogen supply, and downstream conversion, rather than the efficiency of individual units alone. With appropriate technique, engineering, energy and economic boundaries, this pathway has potential for large-scale demonstration and may become an important complement to coal power

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decarbonization.

Keywords: carbon capture; hydrogen production; syngas generation; syngas conversion; certification and economics of e-fuels

引 言

燃煤发电长期以来一直是我国能源结构的主导力量。2025年,燃煤发电装机容量为15.4亿千瓦,发电量为63271.5亿千瓦时^[1]。在“双碳”能源转型背景下,由于电力生产已从燃煤发电转向可再生能源发电,因此燃煤发电装机容量和发电量占比逐年下降。但在2025年,燃煤发电占比仍为59.8%(2015年为73.2%)。燃煤发电在一次能源消费中的占比仍然超过50%,如此高的比例决定了燃煤发电难以在长期内完全退出市场。然而,燃煤机组的碳排放量巨大。全国燃煤发电单位二氧化碳排放量为924克/千瓦时^[2],这是实现“双碳”目标的关键难点。同时,2024年7月,国家发展和改革委员会、国家能源局印发《煤电低碳化改造建设行动方案(2024–2027年)》,协调现有燃煤机组的低碳转型和新建燃煤机组的低碳建设,以提高煤炭的清洁高效利用,加快构建清洁、低碳、安全、高效的新能源体系。

随着新能源体系逐步扩大,二氧化碳也不应只被看作待处理的废弃物,而在一定条件下还可以转化为碳资源加以利用。通过将CO₂作为碳源介质进入化学转化和储能过程后,有机会在减排之外生产燃料和化学品,形成碳资源增值的新路径。其中,碳捕集(Carbon Capture, CC)构成煤电减排链条中的前端基础技术。CC技术一方面可对煤电厂排放的CO₂进行规模化捕集,另一方面以碳介质接入下游加氢转化过程,制备航空煤油(e-kerosene)、甲醇(e-methanol)等合成燃料(e-Fuels)。

目前我国的煤电厂的排放特征为碳捕集与CO₂转化提供了较好的现实条件。一方面,我国典型现役煤电单机参数高,容量大。2023年超超临界和超临界机组占比合69%,600 MW及以上机组占比55%,后燃烧的烟气CO₂浓度约为10%–15%,具备规模化捕集的可行性;另一方面,燃煤电厂目前执行的GB13223–2011火电厂超低排放(Ultra Low Emission)标准已经将烟尘、SO₂、NO_x的排放标准分别降低5 mg/Nm³、35 mg/Nm³、50 mg/Nm³,严格的国家排放标准为CC技术提供了干净的原料气,使下

游利用环节降低了能耗,也避免了CO₂加氢催化剂的中毒失活的问题。

综上,本文将全面考察“CC to Fuels”技术链及其工程制约因素。文章从碳源和氢源获取、合成气生成与转化、产品分离与精炼等环节入手,比较了不同技术路线的适用性、成熟度差异以及关键问题。最后,结合国际政策认证、全生命周期减排要求和经济制约因素,分析了该技术从技术可行性研究到工程应用的主要挑战。

1 系统边界

由于本文旨在尽可能真实地反映产业化水平,因此系统边界的范围较广。图1展示了本文所涵盖的系统边界范围,包括从上游到下游的整个产业链。具体而言,系统边界主要包括五个核心环节:(1)氢源获取;(2)碳源获取;(3)合成气生成与转化;(4)产品分离与精炼;(5)燃料储运与利用。

在“碳源获取”环节,目前煤电行业较常用的CO₂捕集途径为化学吸收法,其中使用单乙醇胺(MEA)溶液作为吸收剂的工艺工程基础较成熟。图2展示了适用于煤电厂的常规CO₂捕获工艺示意图。烟气经预处理后进入吸收塔,与逆流喷淋的吸收溶液接触,CO₂被吸收并生成含有碳酸氢盐或碳酸盐等的富液;富液之后在再生塔中加热分解,释放高纯度CO₂并得到再生贫液回流循环。其主要输入为烟气、再生蒸汽与驱动电能,主要输出为纯度可达98%以上的CO₂及循环使用的溶液。

在“氢源获取”阶段,目前常用的制氢方法包括蒸汽甲烷重整、生物质转化和水电解。其中,水电解具有氢气纯度高,且作为新能源绿电的下游出口受到重视。其主要原料为水和可再生电力。图3所示为适用于工业应用的碱性水电解制氢工艺示意图。原水首先经过脱盐和净化处理后进入给水单元,与KOH碱性溶液混合形成电解液,然后由循环泵送入电解槽。电解槽组由多个电解单元组成。在直流电源供电下,水在阴极被还原为氢气,在阳极被氧化为氧气。生成的气液混合物流经气液分离器,分离出氢气、氧气和电解液。电解液被循环

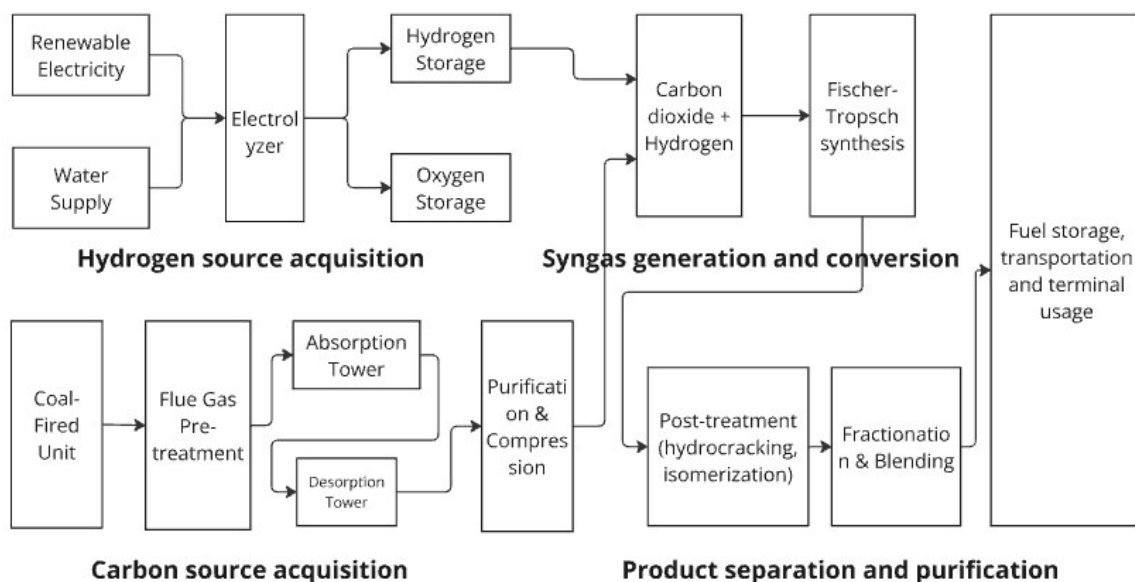
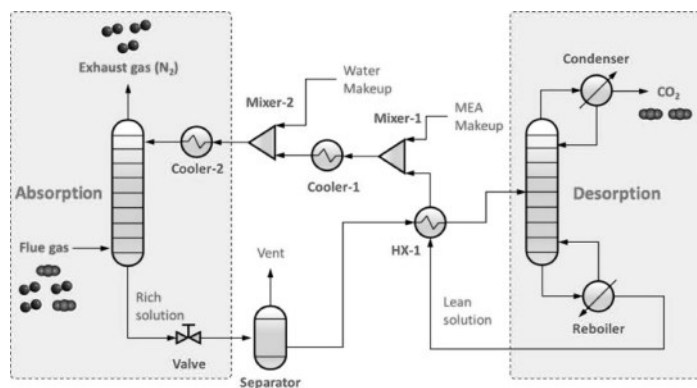


图1 系统边界下的“CC to e-Fuels”全链物质流程图

Fig. 1 Process flow diagram of "CC to e-fuels" chain considering system boundaries

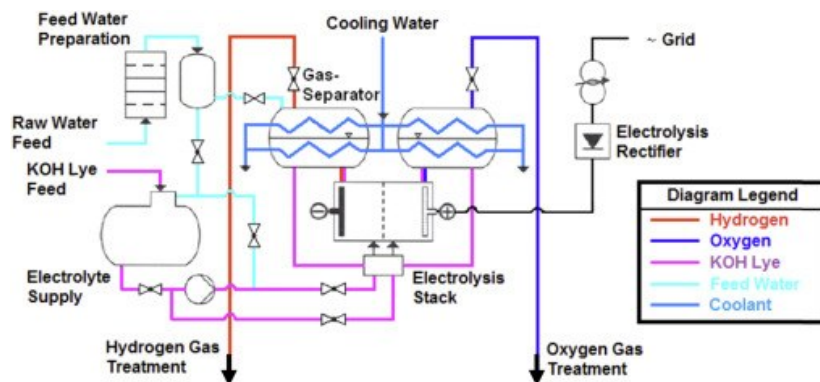
图2 适用于煤电厂的常规CO₂捕获工艺示意图^[3]Fig. 2 Schematic diagram of a conventional CO₂ capture process for coal-fired power plants^[3]

回电解槽重复使用。其整体能量效率通常为60%~75%,因此需要冷却水去除多余的热量。生成的氢气在进入氢气处理单元之前,需经过冷却、干燥和净化处理。通过后续压缩,其压力可增至3~4 MPa,以满足后续e-Fuels的反应要求。副产物氧气也可作为工业副产品回收利用。该工艺路线是目前用于CC to e-Fuels的绿色制氢的可行方案之一。

在“合成气生成与转化”环节,捕集的CO₂与氢气需通过化学转化形成可用于下游e-fuels的合成气。合成气生成的路线主要有(1)逆水煤气变换(RWGS)-费托合成(FT)路径;(2)甲醇中间体路径(MTJ);(3)直接液体烃合成路径。其中,RWGS-FT路径是较为成熟的路线。其基本思路是通过RWGS将CO₂转化为合成气(CO+H₂),再经费托

(FT)反应生成C₁-C₄气体、C₅-C₃₀烃类及高碳蜡油。MTJ是近年受到较多关注的间接路径。该路线先以Cu-Zn-Al催化剂合成甲醇,再通过甲醇经低碳烯烃制喷气燃料。直接液体烃合成路径是意在通过新型多功能催化剂体系(如双功能金属-酸催化剂)实现CO₂的一步转化,直接生成符合航空燃料碳链分布的液体烃。

在“产品分离与精制”环节,e-Fuels的粗产物为宽馏分混合烃,需经冷凝、分馏及加氢处理得到目标产品,如符合ASTM D7566标准规范的合成航空燃料。随后通过分馏塔实现轻组分(汽油馏分)、中间组分(航煤馏分等)与重组分(蜡油等)的分离。由于费托分布规律限制,直馏航煤馏分收率仅约25%-40%,因此需对高碳蜡油进行加氢裂化与异

图3 适用于工业场景的典型碱性水电解制氢工艺示意图^[4]Fig. 3 Schematic diagram of a typical alkaline water electrolysis process in industrial scenarios^[4]

构化,将长链烃裂解,使航煤收率和品质提升。此环节决定了航煤品质与产率,是CC to e-Fuels走向产业化时必须解决的环节。

在“储运与终端使用”环节,e-Fuels通常采用常压储罐、管道或槽车运输,这部分能耗在全链条中占比最小(通常不足5%)。在终端燃烧阶段,e-Fuels,如航煤的高位热值约为42~44 MJ/kg,其燃烧排放仍以CO₂和H₂O为主,但由于原料端已通过碳捕集形成循环利用,故全生命周期的碳排放可明显下降。

2 技术进展

2.1 碳捕集技术

碳捕集(CC)是CC to e-Fuels体系的前端环节。根据碳源浓度和气体性质的不同,碳源可分为三类:

(1)高浓度点源,如燃煤电厂、钢铁、化工及水泥工业生产的排放气,CO₂浓度通常在4~30%;

(2)低浓度扩散源,如交通尾气及建筑通风排放,CO₂浓度通常在0.1%~10%;

(3)超低浓度空气源,CO₂浓度仅约0.04%。

煤电厂在不同工况下可涵盖上述三类碳源形态,因此需要根据工况与碳源的差异性,采取不同的捕集方式。表1给出了主流的二氧化碳捕集技术。

目前,二氧化碳捕集技术可根据碳源浓度、分离机理与应用工况的不同,可分为燃烧后捕集(Post-combustion Capture)、燃烧前捕集(Pre-combustion Capture)、过程内捕集(In-situ Integrated Capture)和空气捕集(Direct Air Capture, DAC)四大类。

燃烧后捕集是现阶段应用范围最广、工程经验也最充分的路线,主要包括化学吸收(Chemical Absorption)、物理吸附(Physical Adsorption)、膜分离(Membrane Separation)等方法^[5]。化学吸收法利用吸收剂与CO₂之间的可逆化学反应进行分离,在工业装置中应用较多^[6]。目前,电力行业的碳捕集成本约为200~600元/吨CO₂^[7]。典型吸收剂如单乙醇胺MEA、MDEA、氨基酸盐及离子液体,具有较高的吸收选择性和分离效率^[8],但其再生能耗高^[9]、溶剂腐蚀性和热稳定性较差^[10]。不过,再生能耗可经“级

表1 不同场景下CO₂捕集的主流技术路径Table 1 Mainstream Technologies for CO₂ Capture in Different Scenarios

捕集路线	英文名称	典型技术	适用对象	主要特点
燃烧后捕集	Post-combustion Capture	化学吸收、物理吸附法、膜分离法	燃煤电厂、工业烟气	适用于中低浓度烟气,改造适应性强,但再生能耗高
燃烧前捕集	Pre-combustion Capture	气化→水煤气变换→吸收/膜分离	煤气化、天然气重整制氢	在燃烧前将碳转化为高浓度的二氧化碳,有利于分离
直接空气捕集	Direct Air Capture	高温液体吸收法 低温固体吸附法	大气二氧化碳	不依赖固定排放源,但气源浓度低,能耗和成本较高
过程内捕集	In-situ Integrated Capture	富氧燃烧捕集法 化学链燃烧法	燃烧或转化过程耦合	捕集过程与反应/燃烧过程耦合,有利于提高系统集成度

间冷却+富液分流+贫液闪蒸 压缩工艺”的节能改造后可从 4.0 GJ/t- CO_2 降低至约 2.4 GJ/t- CO_2 ^[11],或利用气提促进强化 CO_2 解吸过程^[12]等技术降低;而溶剂腐蚀性和热稳定性可利用金属离子^[13]、复合胺^[14-15]、碱金属水溶液^[16]、悬浮纳米颗粒^[17]和冷冻氨水^[18]、离子液体^[19]、强化结晶氨法^[20]等新型吸收剂改善,这也是近年研究较集中的方向。

燃烧后捕集中,近年较受关注的改进方向是相变吸收剂(phase-change absorbents),尤其是可发生液液或固液分相的胺基双相吸收剂等^[21]。该类体系在吸收 CO_2 后可自发形成富 CO_2 相和贫 CO_2 相,从而减少需要进入再生塔的液体体积,也可有利于降低再生能耗^[22]。如 DETA+DMSO+ H_2O 相变吸收剂在二氧化碳吸收容量(3.17 mol CO_2 /kg 溶剂)和解吸容量(2.13 mol CO_2 /kg 溶剂)方面均优于 MEA 吸收剂,其再生能耗仅为 MEA 的 29%^[23]。相变吸收剂开发时需要确保 CO_2 富集相的比例和粘度达到最佳状态。过高的 CO_2 富集相会限制其节能的效果,而过高的粘度则会阻碍传质速率,最终影响吸收性能^[24]。目前,相变体系距大规模工程应用仍存在距离,主要瓶颈包括长期稳定性不足、分相行为与传质行为耦合机理尚不清晰、溶剂降解与挥发数据不完备等^[25-26]。

物理吸附法则利用多孔材料表面对 CO_2 分子的范德华力或静电作用实现可逆吸附。由于不形成新的化学键,所以此法是一种典型的低能耗分离技术(通常<1 GJ/t CO_2)^[27]。常用吸附材料包括碳质多孔活性炭^[28]、碳分子筛^[29]、石墨烯^[30]与非碳质的沸石^[31]、金属有机骨架(MOFs)^[32]以及二氧化硅基材料^[33]等。这些材料的吸附性能取决于其孔径分布^[34]、比表面积^[35-36]、表面极性^[37-38]以及化学官能团^[39]类型。碳质的活性炭与非碳质的沸石与二氧化硅基材料在常压下吸附量在 0.5-5 mmol/g 量级^[40-41],而石墨烯或 MOFs 在 30 bar 的压力下吸附量一般可达 20-60 mmol/g 量级^[42-43],迄今为止记录到的晶体材料中最高的表面积 MOF-210 由 Yaghi 等^[44-45]开发,活性表面积为 6240 m^2/g ,二氧化碳吸附量为 65 mmol/g。

此外,物理吸附过程通常发生在较低温度下(20-60 $^\circ\text{C}$)^[46],并在解析(Desorption)阶段可通过减压或真空压力变换吸附(Pressure Swing Adsorption, PSA/Vacuum Swing Adsorption, VSA)^[47]、升温(Temperature Swing Adsorption, TSA)^[48-49]等实现 CO_2 释放。近年的研究已不再局限于提升比表面积,而

是转向位点化学、孔径调控和耐湿稳定性的协同设计,例如在 MOFs 中引入疏水性官能团或在多孔碳表面负载胺类分子,以兼顾高选择性与耐湿性^[39,50],通过调控沸石的骨架的组成和结构和阳离子交换^[51-52],可以显著强化二氧化碳的吸附能力等。

膜分离(Membrane Separation)技术基于气体分子在膜材料中溶解和扩散速率的差异,可实现连续分离,具有结构紧凑和运行灵活的优势^[53-54],目前工业上主流的气体分离膜主要包括橡胶状聚合物和玻璃态聚合物^[55]。膜分离本身能耗较胺吸收法低^[56]。但高选择性的聚合物膜渗透性较低,反之亦然,此外,当前传统膜材料还面临污染易堵塞物理老化等问题^[57-58],需要进一步通过在膜捕集前增加二氧化碳浓度^[59]、交联形成化学键^[58]或在渗透侧施加真空^[60]等手段来实现高回收率和高纯度。因此近年来,膜分离也从传统聚合物膜逐步拓展到 MOF/聚合物混合基质膜(MMMs),它具有独特的气体分离性能,机械强度,正逐渐成为解决这类问题的新兴方案。目前已经开发出多种包括多孔有机聚合物(POP)、超交联聚合物(HCP)、固有微孔聚合物(PIMs)、热重排聚合物(TRPs)和聚酰亚胺(PIs)、交联聚氧化乙烯(PEO)等的微孔有机材料膜及其复合体系^[61-62]。这类新材料有可能同时改善 CO_2 渗透性与选择性,并为小型化、模块化部署提供材料基础^[63],因此适合与分布式碳源和柔性 e-Fuels 前端捕集相结合。

燃烧前捕集多用于煤气化或天然气重整过程^[121]。该路线先将燃料部分氧化生成 CO 与 H_2 ,并经变换反应($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$)后^[64],用物理吸收或膜分离技术去除 CO_2 。该方法能耗较低、捕集效率高,适合与合成气制燃料或发电厂过程集成,如整体气化联合循环工厂(Integrated Gasification Combined Cycle, IGCC)等^[65],但其工艺复杂、设备投资较大,主要用于大型化工或能源装置,目前 IGCC 工厂的净发电量规模在 120 到 2400 MW^[65]不等。

过程内捕集通过调整燃烧过程本身来实现 CO_2 的富集。代表性路线包括富氧燃烧捕集(Oxy-fuel Combustion)和化学链燃烧(Chemical Looping Combustion, CLC)。富氧燃烧通过使用纯氧或高氧空气代替普通空气助燃,使燃烧产物主要为 CO_2 和 H_2O ,冷凝除水后即可获得高浓度 CO_2 (70-95%)^[66],避免了空气中 N_2 的稀释效应^[67]。该方法流程简单、 CO_2 浓度高,易于与下游 e-Fuels 合成耦合,但受制

于空分制氧系统能耗高^[68],但可与电解水制氢副产氧气结合解决。化学链燃烧则在高温下将金属氧化物(如 Fe_2O_3 、 NiO 、 CuO 等)作为氧载体^[69],使用空气代替纯氧,实现燃料的间接氧化,在反应过程中天然分离出 CO_2 和 H_2O ,具有较高的热效率和产物纯度。但氧载体的循环稳定性和经济性仍是研究重点与瓶颈^[70]。需要指出的是,CLC近年已从材料和小试研究逐步走向工程示范:东方电气集团与清华大学团队在国际上首次成功实现了5 MW_{th}化学链燃烧系统系统自热连续运行,表明该技术正在向更高技术成熟度推进^[71-72]。但从工业化角度看,氧载体磨损与失活、灰硫杂质耐受性、固体循环稳定性^[70]、反应器气固流动放大以及系统可靠性仍是决定其能否真正嵌入大型“CC to e-Fuels”系统的核心挑战。

近年来,直接空气捕集作为一种从大气等超低浓度中直接获取 CO_2 的技术,成为碳中和体系中的

重要绿碳来源^[73],在碳中和框架下具有负碳价值。如图4所示,DAC系统主要分为两类技术路线:一类为高温液体吸收法,通常采用碱性溶液(如 NaOH 、 KOH)在高温条件下与 CO_2 反应生成碳酸盐^[74];另一类为低温固体吸附法,依托胺功能化多孔材料(如MOFs)或碳酸盐循环体系在较低温度下实现可逆吸附^[75]。但由于大气中 CO_2 含量仅约0.04%,系统运行的能耗与成本仍然较高。现有分析认为,高温液体吸收与低温固体吸附的总能耗大致相当,约为 $6.7 - 7.0 \text{ GJ} \cdot \text{t}^{-1} \text{ CO}_2$ ^[74],其中电能与热能消耗占比为2:8,总捕集成本约为 $94 - 232 \text{ USD} \cdot \text{t}^{-1} \text{ CO}_2$ ^[73-74]。因此,提升吸附剂的循环稳定性、降低再生能耗并实现可再生能源驱动仍是DAC商业化的关键。国际上典型代表企业包括瑞士Climeworks^[76]、加拿大Carbon Engineering^[77]与美国Zero Carbon Systems^[78]等,其多个示范项目验证了DAC在未来碳循环体系中的应用潜力。

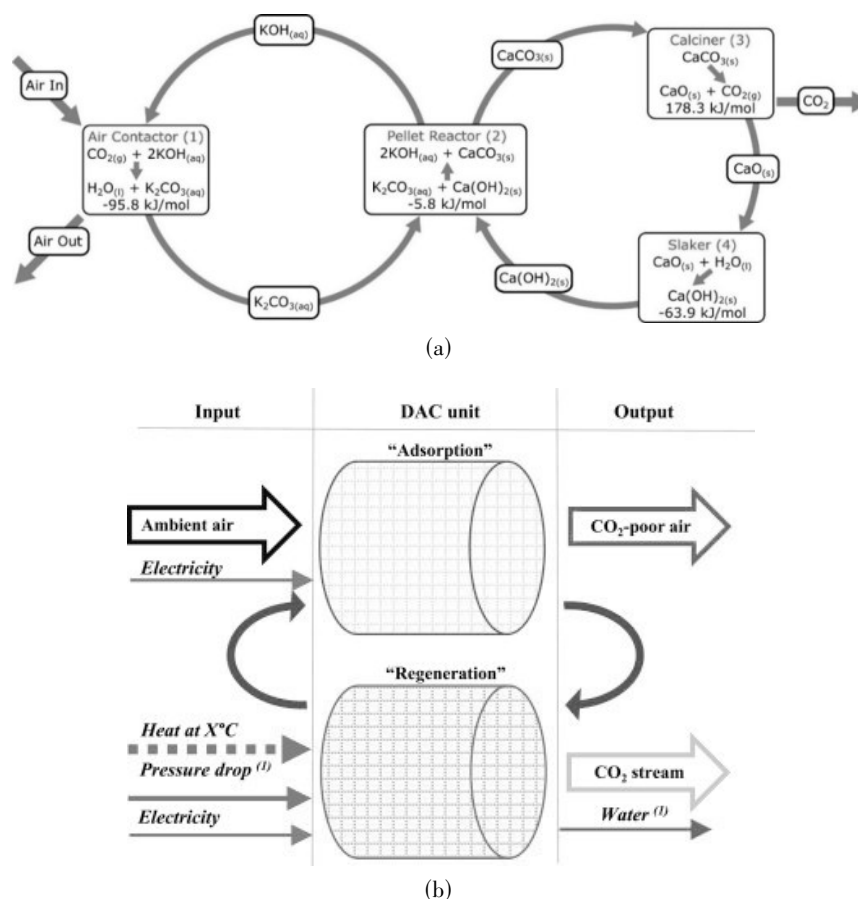


图4 用于直接空气捕集:(a)高温液体吸收法^[74];(b)低温固体吸附法^[79]

Fig. 4 Technical methods for DAC: (a) high-temperature liquid absorption^[74]; (b) low-temperature solid adsorption^[79]

此外,捕集与利用一体化(Integrated CO₂ Capture and Utilization, ICCU)已成为该领域较值得关注的方向^[80-81]。与“先捕集一再提纯压缩一再输送一后转化”的串联流程相比,ICCU试图通过双功能材料(DFM_s)^[81]、反应吸收体系或耦合电化学装置^[82],在同一单元或紧耦合系统中完成CO₂捕集与转化。ICCU的核心思想并不只是流程合并,而在于将吸附位与催化/电催化位进行空间和热力学匹配,使捕集态CO₂直接经历甲烷化、逆水煤气变换或电还原生成CO/合成气,从而减少中间压缩、纯化和传质阻力,并提高低浓度碳源接入甲醇、合成气或甲烷路线的可行性^[80,82]。近期分析认为,热驱动DFM_s体系已可在吸附与反应循环中实现捕集CO₂向CO或CH₄的原位转化,电化学耦合体系也已实现捕集液中CO₂的连续释放与电解协同,并稳定输出适于下游燃料合成的合成气^[81-83]。其主要瓶颈在于:吸附位与活性位匹配不足会导致CO₂结合过强而难以活化、或迁移过慢而限制反应速率;同时,真实烟气中的H₂O、O₂、SO_x和NO_x也会同时干扰捕集容量、界面酸碱平衡,影响催化稳定性;此外,循环工况下的热管理、反应器构型、材料衰减与动态负荷响应仍决定其能否由实验室走向连续工程运行^[80-81,83]。总体看,ICCU是最契合“CC to e-Fuels”对流程紧凑化与能质协同的要求的技术,但目前仍处于由材料可行性验证向系统工程集成过渡的阶段。

由此来看,碳捕集技术正从提高单一工艺的效率转向涉及材料创新、工艺强化和系统耦合的协同设计。对于CC to e-Fuels系统而言,关键不再是单

一捕集路径的优势,而是针对不同的碳源条件,采用不同的捕集方式:高浓度点源适用于吸收法及其相变升级路径;中高压工艺气体适用于燃烧前分离和膜强化;分布式灵活场景适用于先进膜和模块化吸附单元;而长循环低碳闭环系统则更多地依赖于直接空气捕获(DAC)和内部碳捕获与转化(ICCU)的协同支持。

未来的CC技术更新可以将碳捕集与碳转化耦合起来,通过碳捕集用的吸收剂和碳转化用的催化剂,两者协同来实现反应与内部能量循环的集成;其次,可以利用低品位热能,如工业废热或太阳能热化来降低再生能耗;再者,可以通过模块化分布式部署,构建灵活的小型化单元,以实现碳流与可再生能源系统之间的闭环。

2.2 氢获取技术

氢气属于“CC to e-Fuels”体系中的关键能量载体与还原剂,其制备方式会直接影响e-fuels的碳中性水平。表2给出了不同碳排放下H₂获取的主流技术路径。根据来源和碳排放特征,可将氢气分为灰氢、蓝氢与绿氢三类。灰氢通常来源于化石燃料重整,如天然气蒸汽重整或煤气化过程,虽然成本低,但伴随大量CO₂排放;蓝氢在灰氢技术路线上引入碳捕集与封存利用技术,可显著降低碳排放;而绿氢则通过可再生电力驱动电解水反应获得,是实现“CC to e-Fuels”体系真正碳中性的根本途径。考虑到绿氢在CC to e-Fuels体系碳减排中的关键作用,本文主要讨论电解水制氢相关技术路线。

表2 不同碳排放下H₂获取的主流技术路径

Table 2 Mainstream technologies for H₂ production under varying carbon emission scenarios

氢源类型	主要来源	代表过程	典型过程	碳排放特征
灰氢	化石燃料重整或气化过程	煤气化、天然气重整、重油部分氧化	$C + 2H_2O \rightarrow CO_2 + 2H_2$ $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	二氧化碳直接排放,低碳属性弱
蓝氢	化石燃料重整或气化过程+碳捕集封存与利用技术	煤气化或天然气重整耦合二氧化碳捕集	H ₂ production + CO ₂ Capture storage/utilization	依赖碳捕集,相比灰氢可降低过程碳排放
绿氢	水+可再生能源	AWE、PEMWE、SOEC、MEC	$2H_2O \rightarrow O_2 + 2H_2$	制氢过程碳排放最低

根据电解质种类与离子传导机制的不同,电解水技术主要分为碱性电解(Alkaline Water Electrolyzers, AWE)、质子交换膜电解(Proton Exchange Membrane Water Electrolyzers, PEMWE)、固体氧化物电解(Solid Oxide Electrolyzer Cell, SOEC)和微生物电解池(Microbial Electrolysis Cell,

MEC)四类。表3给出了不同电解技术的差异。

近年来,AWE的研究重心从传统的低成本大规模制氢^[102]逐步转向“高电流密度^[103-104]”和“可再生能源友好型^[105-106]”运行模式。在材料方面,Cu/Ni/NiZn-PtRu阴极^[86]、NiFe-(羟基)氧化物阳极^[87]、Ru/Au纳米颗粒^[107-108]等电极的表面工程与多孔结构优

表 3 不同电解水技术的比较^[84-85]Table 3 Comparison of different water electrolysis technologies^[84-85]

	AWE	PEMWE	SOEC	MEC
电极反应	HER $2\text{H}_2\text{O}+2\text{e}^-\rightarrow\text{H}_2+2\text{OH}^-$ OER $2\text{OH}^-\rightarrow\frac{1}{2}\text{O}_2+\text{H}_2\text{O}+2\text{e}^-$	$2\text{H}^++2\text{e}^-\rightarrow\text{H}_2$ $\text{H}_2\text{O}\rightarrow\frac{1}{2}\text{O}_2+2\text{H}^++2\text{e}^-$	$\text{H}_2\text{O}+2\text{e}^-\rightarrow\text{H}_2+\text{O}^{2-}$ $\text{O}^{2-}\rightarrow\frac{1}{2}\text{O}_2+2\text{e}^-$	$2\text{H}^++2\text{e}^-\rightarrow\text{H}_2$ $\text{CH}_3\text{COO}^-+\text{H}_2\text{O}\rightarrow\text{CO}_2+\text{H}^++\text{e}^-$
隔膜	由石棉等陶瓷氧化物和聚合物制成; 30%~40%浓度的氢氧化钾(KOH)	固体聚合物电解质(SPE), Nafion或Aquivion等	固态氧化物(如钇稳定的氧化锆(YSZ))等	低温废水、乙酸盐、生活污水、发酵污泥
电极材料	NiFe-(羟基)氧化物镍基 ^[86-87]	铂、铱、钌和碳载铂 ^[88]	Ni-YSZ、LSCM、LSCF	镍基合金和导电聚合物生物阴极
电流密度	0.2~0.4 A/cm ²	0.6~2 A/cm ² ^[89]	0.3~1 A/cm ²	0.2~A/cm ² (受限于微生物代谢速率)
工作温度	65~100℃	50~90℃ ^[90]	700~1000℃	低温(10℃) ^[91]
工作压力	0.1~30 Bar	15~30 bar ^[92]	atm或略高一些	基本为常压,微生物对压力非常敏感,使代谢效率下降
单元电压	1.8~2.4 V ^[93]		0.95~1.30 V	0.2 V~2.0 V ^[94-95]
规模	单体实现 MW 级,系统实现 GW 级 ^[96]	单体 kW 级,系统部署 GW 级 ^[93]	单体 kW 级	实验室规模、<500 L
HHV 效率	60~80% ^[92]	80~90% ^[89]	90~100%	35~65%
工作原理				
优点	- 商业成熟且经济高效 - 非贵金属催化剂^[97]	- 高效、结构紧凑、响应速度快以及易于与太阳能或风能集成等优点 - 在高压低温条件下提供高纯度氢气 - 比 AWE 有更高的离子电导率、更好的动态响应、更小的系统尺寸以及更少的气体交叉^[89,98-99]	高温运行可以提高反应动力学和整体电解速率	能够利用废水作为底物,同时处理有机废物并产生氢气,使 MEC 符合可持续的水-能源-资源关联战略^[100]
缺点	- 电流密度低 - 碳酸盐积累、气体杂质以及在低压操作下可扩展性有限 - 低通量	- 长期性能和商业可扩展性受到膜降解、催化剂成本和可在可变负载条件下的稳定性等挑战的限制 - 析氧反应(OER)催化剂的降解^[101]	- 材料退化(电极分层、相分离和微观结构不稳定)、 - 机械系统稳定性(SOEC 会受到显著的热梯度影响,从而产生热机械应力,进而导致分层、电极开裂和界面退化) - 成本效益	- 电流密度低 - 产氢效率不高,氢回扩散严重 - 生物群落不稳定,容易退化或失活 - 阳极/阴极的材料易被污染

化^[109]提升了碱性条件下 HER 活性与耐久性;同时,隔膜与电解液向低阻、抗碱稳定性更高的复合材料发展^[110-111],以解决气体交叉与传质阻力之间的权衡、并降低反应过电位和减少欧姆损耗^[112]。此外,高电流密度(>1 A/cm²)^[108]操作和风光直驱^[88]条件下

的频繁启停已成为评价体系稳定性的关键指标。

PEMWE 研究大多围绕“低贵金属化”与“高稳定性”展开^[113]。由于 Pt 和 Ir 等贵金属作为 HER 的催化剂具有优异的活性和高稳定性^[114],但其受制于资源限制导致成本高昂。因此,相关研究主要放在降

低贵金属的用量的同时保持高电流密度耐久运行^[115-116],如采用分散碳纳米颗粒来构建电化学活性表面积^[117-118]、炭黑作为铂基催化剂的载体材料^[114,119]、使用替代电催化剂,如 MoS_2 ^[120]、 RuS_2 ^[121]、钌基电催化剂^[122]等。同时,多孔传输层(Porous Transport Layer, PTL)与催化层-膜界面的结构优化显著改善气液两相管理、电荷传输与耐久性,使电解在高电流密度下的动态运行更加可控^[123-124]。在系统层面,大量研究关注可再生电力波动下的退化机制^[125],包括膜化学稳定性、金属迁移与气体交叉等,以构建可预测的寿命模型^[93]。此外,阴离子交换膜电解水(Anion Exchange Membrane Water Electrolyzers, AEMWE)则融合了AWE与PEMWE的优点,兼具高性能和经济效益^[126]。目前分析认为,更薄的膜、更高的工作温度以及更高交换电流密度的电极材料是电解槽的发展趋势。

SOEC的研究热点主要体现在两条主线:高效共电解($\text{H}_2\text{O}/\text{CO}_2 \rightarrow$ 合成气)与耐久性优化^[127]。共电解由于可直接生成任意 H_2/CO 比例的合成气^[128],已成为CC to e-Fuels一体化系统集成核心环节路线。共电解研究主要围绕副反应(WGSR/RWGS、DIR)的作用机理^[129],以及通过优化操作、结构与材料来降低 CO_2 的扩散阻力与面积比电阻(ASR)以提升性能。现有分析认为, CO_2 的ASR明显高于 H_2O ^[130],WGSR/RWGS在高温下对合成气产率具有显著影响,而气体组成、温度、电极微结构和改性元素(如Fe、Mo)均会影响CO的生成速率与共电解效率^[131-132]。共电解过程中的化学反应与传质机制仍未完全阐明,后续仍需通过数值分析或调控操作条件与材料体系来精准控制^[133-134]。SOEC的材料耐久性优化主要源于高温电解下的微观结构演化,包括Ni基燃料电极的粗化^[135]、迁移与碳沉积^[136],以及YSZ电解质的孔隙/裂纹形成^[137]等。现有研究通过建模与表征揭示了三相界面的密度下降、气体扩散限制和高电流密度对退化有加速作用^[138],但多数工作仍局限于单一材料或短期测试,对 CO_2 电解条件下的长期稳定性理解不足^[133]。未来需在材料设计、界面调控和操作优化方面进一步探索,以抑制结构演化并提升SOEC的耐久性。

MEC技术的近年的研究主要围绕“无膜化”和“废水协同资源高效化”展开^[139-140]。当前大量研究聚焦于单室/无膜MEC,通过减少膜污染、降低电阻与材料成本来提升实际可部署性^[141]。同时,阴极催

化材料向不锈钢^[142]、Ni-Mo^[143]、Co-Mo^[144]等廉价金属过渡,以改善氢析出性能并降低Pt/C的使用量^[145]。另一方面,通过气体扩散电极、传质优化与操作条件调控来抑制氢回扩散和副产甲烷,可以提高氢回收率^[146]。在规模化方面,MEC越来越多地与真实工业废水处理结合,通过实验与模拟构建“污染物去除+能量回收”的微电化学系统,但规模放大后性能衰减、群落稳定性与成本问题仍未解决^[147]。

因此,电解水制氢与e-Fuels路线耦合时,需要特别关注供氢稳定性、能量匹配与系统集成问题^[148]。电解槽的负荷响应需要与可再生电力波动和下游 CO_2 加氢过程相适配,才能保证适当 H_2/CO_2 比例与反应选择性。同时,虽SOEC等高温共电解产生合成气,具有余热整合潜力,但仍需考虑系统的耐久性和能耗。当需要耦合大规模CCUS系统,即需大规模制氢时,水资源可能成为潜在瓶颈。理论上,每制取1 kg H_2 至少需消耗9 kg H_2O ,但考虑到除盐水制备效率(约50%~70%),实际生产1 kg H_2 需消耗原水约13~18 kg。若进一步计及冷却水损失及废水排放,实际总耗水量将达到20~35 kg^[149]。因此,可考虑将费托合成过程的副产水经净化处理后回用于电解,形成物料循环,缓解水资源压力。从系统角度看,应在供氢稳定性、热能回收、杂质耐受性和经济性之间实现相对平衡。

2.3 合成气生成与转化

CO_2 加氢合成e-Fuels的核心是“合成气生成-烃类生成”两级耦合反应过程。图5给出了煤电厂CCUS体系下二氧化碳加氢制e-Fuels的主流技术路径。左侧为“合成气生成”阶段,二氧化碳经逆水煤气变换反应(Reverse Water-gas Shift, RWGS)、二氧化碳重整甲烷(Dry Reforming of Methane, DRM)或一体化耦合反应(RWGS-FT/RWGS-MeOH)转化为含CO与 H_2 的合成气;右侧为“合成气转化”阶段,合成气进一步通过费托合成(Fischer-Tropsch Synthesis, FTS)制取烃类燃料^[150],或经甲醇合成(MeOH)路线衍生出制汽油(Methanol to Gasoline, MTG)或制航煤(Methanol to Jet, MTJ)等多种液体燃料体系,也可通过直接 CO_2 加氢制烃实现单步转化。

在合成气生成阶段,已有研究多集中于提高 CO_2 转化率与CO选择性以及减轻副反应对催化剂的毒化作用。RWGS是成熟度较高的途径。图6(a)给出了RWGS的反应机理图。 CO_2 先在金属/氧

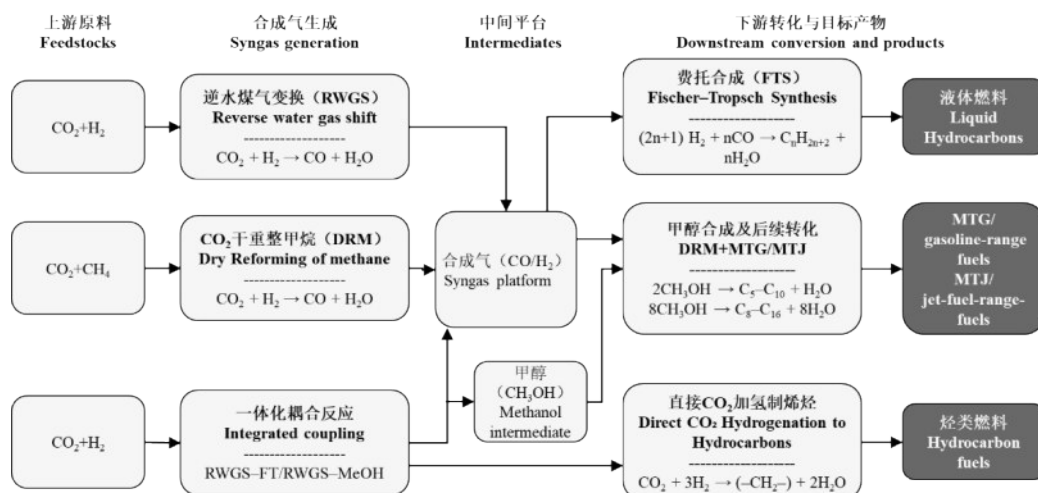


图5 煤电厂CC体系下合成气生成与转化的主流技术路径

Fig. 5 Mainstream syngas generation and conversion technologies within coal-fired power plant cc systems

化物界面吸附活化, H_2 在金属位点解离成 H^* ;之后 CO_2 经 $HCOO^*$ 或 $COOH^*$ 中间体脱氧生成 CO^* ,表面氧/羟基被氢化生成 H_2O ,最终 CO 和 H_2O 脱附,完成 CO_2 向 CO 的转化。相关工作主要围绕新型催化材料设计、机理解析与过程强化三方面:催化剂方面,传统的 Ni 、 Zn 、 Cu ^[151]等金属体系向具有丰富氧空位和可逆氧化还原能力的 CeO_2 ^[152]、 ZrO_2 ^[153]、 TiO_2 ^[154]及其固溶体拓展^[155],通过构建 $Ni/CeZrO_2$ ^[156]、 Cu/CeO_2 ^[157]、 Mo_2C/MgO ^[158]、 $Cu-Fe/CeO_2$ ^[159]等界面结构,降低活化能并抑制甲烷化等副反应;部分工作还发展了过渡金属碳化物(TMCs)^[160]、过渡金属磷化物(TMPs)^[161]与金属-载体强相互作用(SMSI)^[162],以精细调控表面电子结构和反应路径。过程强化方面,电热RWGS、光热RWGS^[163]与等离子体-催化协同^[164]RWGS也受到关注,通过局部高温^[165]、非热激发^[166]或光生电子-空穴^[167]参与,可在400-600℃下获得接近传统高温条件(700-900℃)的 CO 选择性转化率,降低能耗。

DRM因能同时利用电厂周边的煤层气、焦炉气等多碳氢源,成为耦合CC的潜在路径。由于乙烷、丙烷和丁烷等轻烃容易运输,因此也被用于干重整^[168-169]。图6(b)给出了DRMcc。 CH_4 在金属位上裂解,提供 C^* 和 H^* ; CO_2 在金属-氧化物界面活化,提供 CO^* 和 O^* ;其中 O^* 氧化 C^* 生成 CO , H^* 重组生成 H_2 ,最终形成 $H_2/CO \approx 1$ 的合成气。相关工作主要围绕催化剂抗积碳与界面工程方面,通过构建 $Ni-Fe/La_2O_3$ ^[170]、 $Ni-Pd/MgO$ ^[171]、 $Ni-Co/CeO_2$ ^[172]等双金属催化剂及 $Ni-Mo_2C$ 、 $Ni-WC$ ^[173]等碳化物体系,可通过氧空位调控与金属-载体界面电子结构优化来增

强催化剂的抗积碳与结构稳定性。在反应工程方向,等离子体-催化协同^[174-175]、电热/光热耦合^[176-177]以及微通道^[178]、膜反应器^[179]等强化手段可降低DRM的温度需求并提高了过程能效。系统层面,DRM被广泛研究用于与煤电厂 CO_2 捕集^[180]、焦炉气资源化^[181]以及可再生电力的热-电耦合集成,用于实现合成气按需制备与碳减排协同设计。

同时,RWGS与FTS、MeOH合成等下游步骤通过双功能催化剂与一体化反应器(RWGS-FT/RWGS-MeOH)进行热与物质耦合设计,可以在单反应器内实现 $CO_2 \rightarrow CO \rightarrow$ 烃/甲醇的连续转化,并表现出更高的碳利用效率与工艺紧凑性^[182]。图6(c)给出了MeOH的反应机理图。 CO_2 在金属-氧化物界面吸附活化, H_2 解离为 H^* ; CO_2 先形成 $HCOO^*$ 甲酸盐中间体,再逐步加氢为 H_2COO^* 、 H_2CO^* 和 CH_3O^* ,最终 CH_3O^* 加氢生成 CH_3OH ,表面 OH^* 同时生成 H_2O 并再生活性位。催化剂方面,通过将 Cr_2O_3 ^[183]、 Mn_xZr_y ^[184]、 $Zn-ZrO_2$ ^[185]等具备 CO_2 活化能力的金属氧化物,与HZSM-5、SAPO-34、SSZ-13沸石纳米晶^[185]等下游转化位点进行纳米级空间隔离与界面调控,利用不同的活性位点将这两个过程分离。在反应器方面,一体化反应器需满足在同一空间中完成RWGS吸热与FTS/MeOH放热的热量自平衡,目前研究主要集中于蜂窝状微通道^[186]、一体化浆态床与膜反应器^[187]等,意在实现更高的转化率与更均匀的温度分布。

在合成气下游转化阶段,已有研究多集中于提高烃类等目标产物的选择性与可控性、提升催化剂稳定性,以及优化放热反应的热管理。

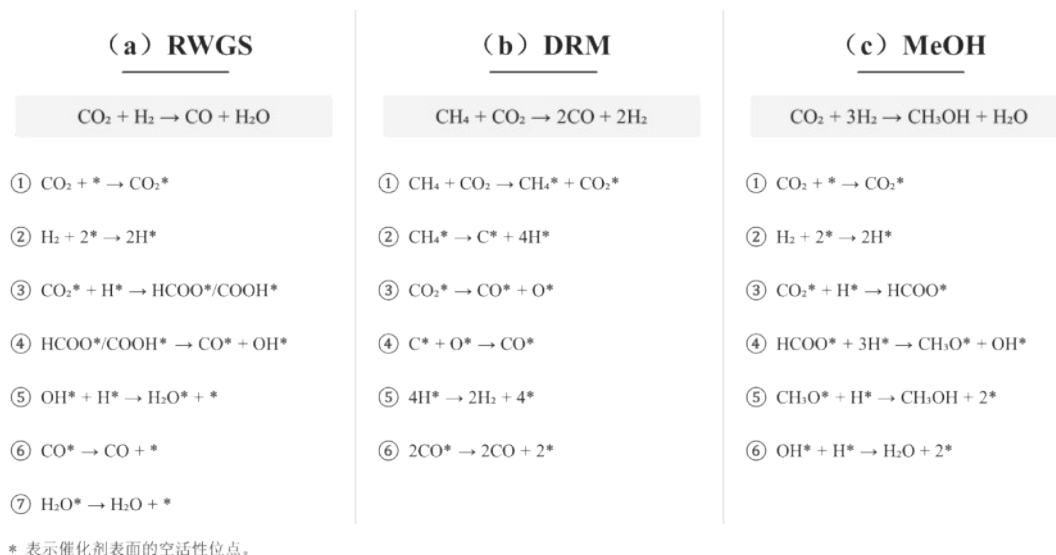


图6 主要合成气生成技术(RWGS、DRM、MeOH)的反应机理图

Fig. 6 Reaction mechanism of main syngas generation technologies (RWGS, DRM, MeOH)

FTS注重长链烃的直接构筑。图7(a)给出了FTS的反应机理图。CO在Fe/Co或碳化铁活性位上吸附并解离为C*和O*；O*被H*氢化生成H₂O，C*被氢化生成CH_x*，之后CH_x*发生C-C偶联和链增长，最终通过加氢终止或β-H消除生成烷烃和烯烃。新型费托合成催化剂主要体现在双金属/合金催化剂、催化剂载体和助剂上^[188]。Co基体系在工业合成长链线性烃方面应用较多^[189]，通常由10-30 wt% Co负载于Al₂O₃、SiO₂、TiO₂等金属氧化物^[190]、介孔^[191]或碳基载体上^[192]，并辅以少量贵金属或过渡金属助剂^[193]。分析认为，钴颗粒尺寸对活性与选择性具有显著影响：过小的Co纳米颗粒(<10-12 nm)易表现为高CH₄选择性和低C₅₊产率^[194]，而颗粒尺寸约在10 nm左右时往往能在活性、选择性与稳定性之间取得较优平衡^[195]，载体孔结构与金属-载体相互作用(MSI)则通过调控分散度、可还原性和传质特征进一步塑造催化性能^[196]。常用助剂(如Pt^[197]、Re^[198]以及Zr、Mn、Ni等过渡金属的氧化物^[199])可通过促进Co₃O₄→Co₀还原、抑制烧结或调控产物分布来提升活性。此外，Co基催化剂的失活主要源于烧结、再氧化、金属-载体强相互作用导致的不可还原物种、孔堵与积碳、中毒及机械磨损等多重机制共同作用。Fe基体系可以生产适用于燃料和化学品的轻烃以及较重的烃类(蜡)^[200]。铁基费托催化剂的特点是价格低廉、适应性强、可根据工艺条件生成不同类型的产物，是煤制油和CO制烃体系中极具吸引力的催化材料。铁在反应过程中会形成

多种铁碳化物(如χ-Fe₅C₂、Fe₇C₃、ε-Fe₂C)^[201]，这些碳化物是费托合成的主要活性相。由于铁同时具有水煤气变换(WGS)活性，能够在反应中自行调节H₂/CO比，因此适合用于H₂含量较低的合成气(如煤气化或CO₂加氢体系)^[202]。在低温费托(200-240 °C)中，铁催化剂主要生成蜡和较长链烃；在高温费托(300-350 °C)中，则倾向于生成汽油组分、轻烯烃和含氧化合物^[203]。Fe基费托催化剂的助剂主要用于调控电子结构和碳化行为，其中K、Na等碱金属可增强CO解离并提高烯烃选择性^[204]，Cu、Mn、Zn等过渡金属改善活性相的分散性^[205]。目前铁基催化剂的主要挑战是其在长期运行时积碳、烧结、活性相变化和机械强度不足^[206]。

甲醇路线可以依托成熟工艺实现可控的燃料分布，如MeOH→MTG/MTJ/MTO/DME/OME等多路径受到关注。图7(b)给出了MTJ/MTG的反应机理图。甲醇先在分子筛酸性位上脱水生成DME，并形成表面甲氧基；之后通过初始C-C键形成进入烃池循环，在烯烃循环和芳烃循环中发生甲基化、低聚、裂化、异构化、氢转移和芳构化。

现有研究更关注通过精细调控分子筛结构与酸性分布来实现目标燃料馏分的定向合成，以ZSM-5、H-ZSM-22、SAPO-11、SAPO-34等分子筛为代表^[207-208]，通过调节布朗斯特酸/路易斯酸比例^[209]、孔径大小、微-介-大孔的体积比^[210]、硅铝比及金属修饰(Ga、Zn、P等)^[211]，实现从轻烯烃→芳构化→低碳异构烷烃等多路径反应网络的选择性导

向,从而精准控制汽油馏分、航煤馏分、轻烯烃及含氧燃料的分布与比例^[212]。尤其在MTJ路线中,最新研究聚焦于直链C₈–C₁₆航煤组分的、高密度燃料的形成机制^[213]以及芳烃/环烷烃比例调控,以同时满足“低凝点、高热值、高能量密度和高十六烷值”等航空燃料关键指标^[214]。此外,MTJ反应机理中C–C重排、异构化与芳构化的竞争关系^[215]成为新的研究重点,通过对骨架中Zr位点分布与框架拓扑的调控等手段来实现异构体分离的策略也逐步成熟^[216]。在DME/OME路线中DME作为氢载体与清洁燃烧燃料^[217],OME则因其超低烟排放与优异喷雾特性被视为下一代航空或柴油替代燃料^[218],利用DME为原料制备OME与其二者的耦合制备逐渐成为CO₂基e-fuels体系的延伸方向^[219],研究热点则聚焦于双功能催化剂结构优化、高选择性一步法工艺、以及OME(尤其是OME1–OME5)组分可控合成^[220]。

直接加氢制烃则试图以更短流程完成CO₂的转化。图7(c)给出了CO₂直接加氢的反应机理图。CO₂直接加氢的本质上是:CO₂和H₂先在金属/氧化

物/酸性复合位上活化,之后CO₂通过RWGS生成CO*并进入CH_x*–C–C偶联–链增长路线,或者通过HCOO*、CH₃O*、CH₃OH/DME等含氧中间体进入烃池路线,最终生成烯烃、芳烃、汽油/航煤范围烃,并伴随H₂O生成与活性位再生^[221]。通过开发负载In基催化剂^[222–223]、K/Fe–C、Co₆/MnO_x、Na/CoCu/TiO₂以及双功能金属–酸性复合体系实现在单一反应器内完成CO₂活化、链增长与选择性调控^[224]。研究热点主要体现在三方面:其一,调控表面CO/H供给比与氧化还原循环以稳定碳化物活性相,提高C₂₊或C₅₊长链烷烃生成选择性^[225–226];其二,采用金属–载体强相互作用(SMSI)调节、氧空位工程、等离子体辅助活化来突破CO₂难活化的瓶颈,提高反应效率^[227–228];其三,通过金属–酸双功能催化剂(如K/Fe–Cu–Al@HZSM-5、NaFe/SAPO-11)实现在一步反应中实现烯烃中间体向异构烃、芳烃及航煤范围烃的可控深度转化,从而为CO₂直接制汽油、柴油及航煤提供可能路径^[229–230]。

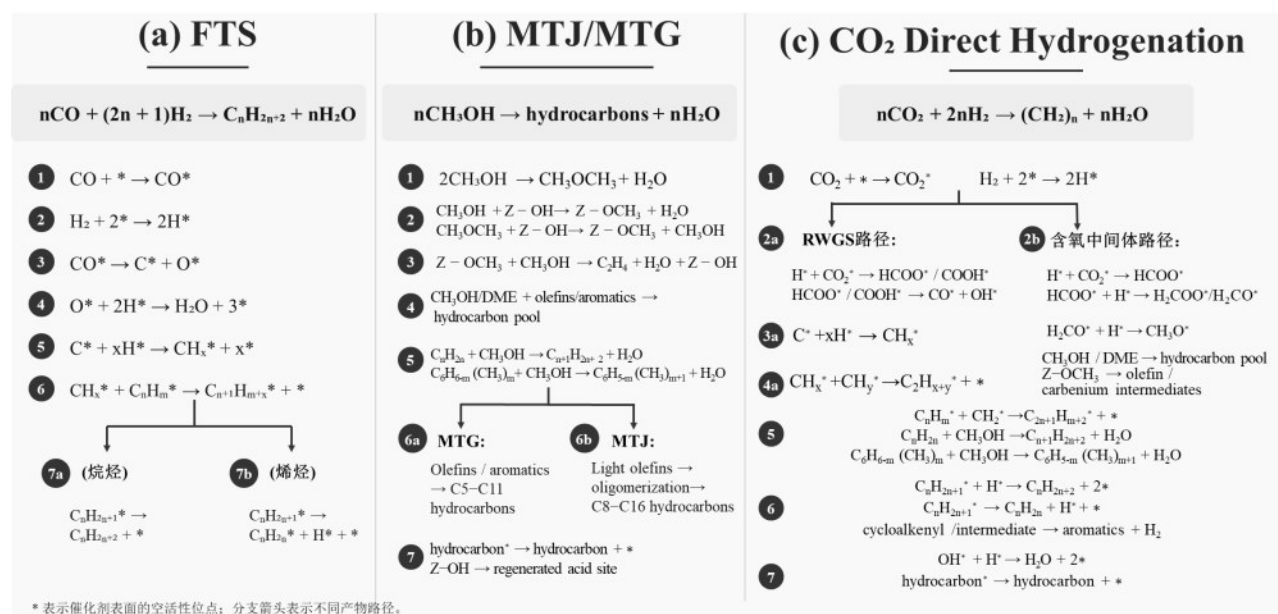


图7 三种主要下游转化技术(FTS、MTJ/MTG、CO₂直接加氢)的反应机理图

Fig. 7 Reaction mechanism of main syngas conversion technologies (FTS, MTJ/MTG, CO₂ direct hydrogenation)

但与RWGS–FT或甲醇中间路线相比,CO₂直接制高碳烃仍处于发展前沿,主要难点在于多步串联反应中各基元过程的速率匹配仍较困难^[187,231]:一方面,CO₂活化、C–C偶联与链增长之间存在竞争,易导致CH₄、CO等低碳副产物增加,限制高碳烃选择性^[231–232];另一方面,双功能体系中金属位点与酸性

位点距离、酸强度及孔道结构对中间体扩散和二次转化高度敏感,稍有失衡即可能引发过度裂化、积碳失活或产物分布偏移^[233–234]。此外,高温含水反应环境下活性金属烧结、碳化物相不稳定及分子筛骨架退化等问题,也使催化剂的稳定性面临挑战^[235]。针对这些问题,近期研究强调从催化剂可控制备入

手提升结构有序性与位点协同性,例如采用浸渍-焙烧、共沉淀和物理混合、溶胶-凝胶、核壳封装、限域组装及原子层级分散等方法,精细调控金属尺寸、界面结构与酸性分布,以促进 CO_2 活化中间体的定向耦合和高碳产物选择性生成^[236-237]。高选择性C-C偶联、高稳定性双功能催化剂设计以及与电解制氢和可再生能源深度耦合的模块化工艺方向发展。

近年来,随着 CO_2 基e-fuels技术的发展较快,用于“合成气生成-合成气转化”两个阶段的反应器系统正从传统稳态装置向强化传质传热、外场耦合与流程集成化方向演进。在RWGS、DRM与FT反应器中开始普遍采用金属泡沫、多孔陶瓷蜂窝与3D打印结构化载体,以提升热管理能力、削弱热点并提高 CO_2 转化^[238-239];同时,微波、等离子体、光热感应等电-热耦合反应器在低温 CO_2 活化中显示出较高能效,以适配分布式可再生能源,成为Power-to-X体系的重要研究方向^[240-241]。FTS反应器由传统固定床向高效散热的浆态鼓泡塔、微通道及膜反应器升级,以提高长链烃选择性并减缓失活^[242-243];MeOH则通过多流化床串联、双功能反应器与反应-分离一体化模式实现对轻烯烃、航煤馏分与芳烃生成的精细调控^[244-245]。总体看,反应器设计正朝着结构可控、外场驱动、动力学匹配与流程耦合的方向快速演变,为未来分布式、可再生能源友好的e-Fuels制备提供了新的工程化基础。

CO_2 加氢制e-fuels的路线选择,需要在反应可控和流程集成之间找到平衡。比如,RWGS-FT和甲醇中间体路线流程较长,但每一步的反应边界相对清晰,便于利用已有工业经验进行放大和优化。直接 CO_2 加氢制烃和RWGS-FT一体化反应器虽然能够缩短流程,但也要求催化体系同时满足 CO_2 活化、链增长、酸性位点调控和稳定性等多重要求。一旦金属位点、酸性位点和传质距离匹配不当,就容易出现碳产物选择性下降等问题。因此,近期工程路线更应重视工业放大和优化,而中长期研究则应围绕一体化催化剂与反应器内的热质耦合展开。

2.4 产品分离与精制

在 CO_2 加氢制e-fuels体系中,产物的分离与精制对于系统节能具有重要意义,其技术水平会直接影响工艺的整体经济性。对于费托合成产物,由于生成物碳数分布宽(通常覆盖 C_1 - C_{30}),传统流程多以多级常压/减压蒸馏为主^[246-247],将轻气(C_1 - C_4)、

汽油馏分(C_5 - C_{11})、航煤馏分(C_8 - C_{16})和蜡油(C_{20})分离,其中航煤馏分通常在180-300℃沸程范围内切割。近年的研究主要关注通过选择性吸附^[248]或近临界流体萃取(NCE)^[249]、隔板塔^[250]等手段降低蒸馏负荷,并提高目标产物的收率。目前,在费托蜡加氢裂解装置中,实验室小规模反应器通常基于Sun/Gambaro模型,采用约225-255℃、30 bar、WHSV 6-12 h⁻¹等操作条件^[251-252],用于动力学参数拟合和机理研究。此外,尿素包合法利用乙醇作为活化剂可以在5℃的条件下从费托合成高温油相产品中高效地分离正构烃^[253]。但在工业炼厂中,典型操作条件更为严苛,通常需要350-420℃、100-170 bar、WHSV 0.5-2.0 h⁻¹,并配合较高氢/油比,才能保证大通量处理和深度转化^[254]。

在甲醇路线(MTG/MTJ)及DME/OME路线中,分离与精制的复杂性主要来自含氧化合物与烃类的共存。MTO/MTJ反应后产物流通常包含 C_2 - C_6 烯烃、 C_5 - C_{16} 烃类、未反应甲醇、水及微量含氧副产物,其中水和甲醇的存在会显著影响后续低聚和加氢单元的稳定运行。传统的MTO产品分离方法是低温蒸馏和碱洗,该方法会产生大量油脂,并影响设备安全^[255-256]。针对这一问题,近年来逐步发展了反应精馏一体化^[257]、吸附脱醇^[258]、在 C_2/C_3 分离中MOF膜分离^[259]等新型技术。由此可见,分离与精制技术正在由传统的高能耗蒸馏向新技术与低能耗的方向发展,目标是在提高e-fuels的收率前提下,降低分离能耗并验证其放大的可行性。

在CC to e-fuels体系中,产品分离与精制决定了前端路线的经济性。FT路线的核心问题不是能否生成液体烃,而是宽碳数分布带来的目标馏分收率、蜡油加氢裂化负荷和循环能耗问题;甲醇路线的优势在于平台分子成熟,但水、未反应甲醇和含氧副产物的存在会增加后续分离和精制难度;直接加氢路线即使实现较高 CO_2 转化率,也可能因低碳副产物比例高、目标馏分集中度不足而削弱全链条效率。因此,对合成燃料路线的评价不能仅看 CO_2 转化率和目标产物选择性,还应把分离能耗、燃料标准符合性等作为同等重要的判断指标。

3 国外政策与认证

e-Fuels(包括e-diesel、e-gasoline、e-methanol、e-DME/OME等)的政策与认证体系目前尚未形成

全球统一标准,目前更多采用“燃料属性与减排属性”的双重评价路径。

在燃料属性层面,e-Fuels通常需符合既有的燃料标准体系要求,即要求e-Fuels在密度、馏程、含氧量及材料相容性等关键参数上与现有燃料体系保持一致。

在减排属性层面,较具代表性的是欧盟委员会颁布的《可再生能源指令(EU) 2018/2001》与其相关补充与更新的法规。该指令构建了再生碳燃料(Recycled Carbon Fuels, RCF)与非生物来源可再生燃料(Renewable Fuels of Non-Biological Origin, RFNBO)的温室气体减排评价体系。法规首次明确提出所有RCF必须在全生命周期尺度下实现不低于70%的温室气体减排率,并以94 gCO₂eq/MJ作为统一的化石燃料对标基准。这说明欧盟已将e-Fuels、Power-to-X燃料和CCU燃料正式纳入交通能源低碳转型的核心技术路径。在法规中,核算温室气体排放的全生命周期方法的计算公式为:

$$E = e_i + e_p + e_{id} + e_u - e_{ces}$$

该公式涵盖了投入供应排放、加工排放、运输分配排放、燃料使用排放,并扣除碳捕集与封存减排量等要素。法规为避免减排量的双重计算,明确不得对某些已在其他欧盟法律下计入的二氧化碳捕集给予重复抵扣。

此外,碳的来源是取得欧盟认证的关键。此法规引入了“刚性输入”和“弹性输入”的碳源分类,以区分原料来源对排放核算的影响。如使用刚性输入(符合RCF定义的废气或不可物质回收的废弃物)制造燃料的话,则相当于避免了其原本要产生的排放,因而计算中允许减去该原料原本的排放;弹性输入(如炼油厂的石油产品,可通过调整产出比例增产)则因为其供应可增可减,通常不能给予此类排放抵扣。需要指出的是,欧盟还将来自化石能源体系的碳源通过CC得到的e-Fuels明确定位为脱碳转型阶段的过渡阶段的重要技术。在当前阶段,由于工业和能源系统中仍存在大量可捕集的二氧化碳来源,碳的具体来源在短期内不做严格的刚性约束,但在迈向2050年碳中和的长期路径中,可利用的碳源将逐步收缩,因此继续使用来自化石能源体系的碳源将构成对化石能源的路径依赖,需要使用直接空气捕集等更加绿色的碳源用作可认证的碳源。

在核算电来源与其碳强度核算方面,该法规引

入了按能量份额分摊的方法。当同一工艺同时产出RFNBO和RCF时,需要根据各自“相关能量投入”占总能量投入的比值来划分产出的燃料类别比例。例如,使用可再生电力产生氢气与化石废气合成燃料时,可再生电力的能量占比决定该燃料中视为RFNBO的份额,废气投入的能量占比决定RCF的份额,从而分别计算其减排强度。这一方法有助于解决Power-to-X与工业尾气协同转化等复杂耦合系统中燃料减排属性的问题,为e-Fuels的工程建模提供了可操作的制度边界。

4 体系经济性与工程化挑战

从工程落地看,煤电厂CC to e-Fuels路线的瓶颈并不来自单一环节,而是由碳氢成本、装置利用率与系统效率等共同决定。首先,绿氢成本是最主要的成本项^[260]。现阶段碱性电解制氢成本大致在5-7USD/kg-H₂,IEA则指出,电解槽系统投资在不同地区仍然较高,中国约为600-1200 USD/kW,中国以外约为2000-2600 USD/kW^[261]。且电解槽设备本体通常只占总投资的一部分,工程、采购、施工与其他配套支出会显著抬高系统投资^[262]。因此,e-Fuels属于“高资本投入、低原料价格”的项目,其平准化燃料成本可写为:

$$LCOF = \frac{CRF \cdot CAPEX + OPEX_{fix}}{M_{fuel}} + c_{H_2} m_{H_2} + c_{CO_2} m_{CO_2} + c_{el} E + c_{heat} Q$$

其次,氢耗与碳效率直接影响了原料成本。若将目标液体烃近似写为(CH₂)_n,则理论上每生产1 kg液体烃,理论最低需要0.429 kg H₂和3.143 kg CO₂。但实际流程中,由于RWGS平衡、尾气循环、轻气副产物、未反应物分离回收以及放空损失,真实需求明显更高。已有FT型PtL研究给出的代表性流程中,223 t/d H₂与2387 t/d CO₂仅产出351 t/d液体燃料,折算为每1 kg fuel约消耗0.635 kg H₂和6.80 kg CO₂;换言之,实际氢耗约为理论值的1.48倍,CO₂需求约为理论值的2.16倍^[263]。若按DOE当前5-7 USD/kg-H₂估算,仅氢这一项就对应3.18-4.45 USD/kg-fuel的原料成本;相比之下,即使按我国电力行业200-600元/t-CO₂的捕集成本估算^[7],CO₂原料项大致还有1.36-4.08元/kg-fuel。这说明在当前阶段,捕集费重要,但氢耗和碳效率才是决定项目经济性的第一约束。

更需要注意的是,系统总能效偏低会使资本投

入与电耗被放大。近期针对 FT 型 PtL 流程的系统评估显示,依据 CO₂ 来源与工艺集成方式不同,PtL 总效率约为 54.7% - 63.8%,而碳效率仅为 68.4% - 88.6%^[264],而另一项 power-to-jet-fuel 研究给出的 power-to-kerosene 效率为 38.71%,整体能效约 48.06%^[254]。这也说明,为了得到 1 单位液体燃料,前端必须输入远高于燃料热值本身的电能和氢气,并配置更大的电解、捕集、压缩和合成装置。换言之,系统效率每下降一点,不只是多耗一点电,而是会连带放大电解槽规模、CO₂ 捕集量、压缩功和反应器负荷,从而整体抬高资本支出与运行费用。

已有技术经济分析认为,e-fuels 的平准化成本对电价、装置利用率及电解技术选择高度敏感。其中 e-kerosene 在基准情景下约为 5.12 EUR/kg,在不同情景下可波动于 0.5 - 6 EUR/kg^[254]。而面向欧洲的 PtL-SAF 在较乐观条件下,2030 年最低成本仍约 1.21 EUR/L (1510 EUR/t),约为历史化石航煤价格的 3 倍^[265]。相比之下,中国的 e-fuels 技术经济性则更具有优势。在 0.3 元/(kW·h)绿电、320 元/t·CO₂ 等主要经济指标下,CO₂ 加氢制 e-methanol 生产成本接近 3.950 元/t。若未来 5 年,绿电和 CO₂ 价格将分别可降至 0.1 元/(kW·h)及 200 元/t 水平,同时考虑到甲醇合成催化技术进步带来的工艺优化,CO₂ 加氢制 e-methanol 生产成本可降至 1.618 元/t,相比当前下降 59%^[266]。这也说明,对于中国煤电 CC to e-Fuels 体系而言,决定经济性的仍然是低成本绿电、低成本绿氢与高利用小时数的协同实现,而不只是单一反应效率提升^[266-267]。

从工程落地看,规模化示范至少有三类问题需要解决。第一是系统的动态匹配问题。上游电解制氢需要能够适应电力波动,而下游 RWGS、甲醇合成和费托合成通常更适合在相对稳定的进料条件下运行。当氢气流量、温度和压力频繁变化时,反应器内的传热传质过程、催化剂表面状态以及产物分布都会受到影响,从而增加操作控制难度,并带来产品质量波动风险^[266]。第二是热量协同利用问题。CO₂ 捕集再生需要中低品位热,RWGS 属于吸热过程,而甲醇合成和费托合成则释放大反应热。若不同单元之间的热量品位、供需时序和负荷变化不能有效衔接,系统往往需要额外补充蒸汽、电加热或冷却设施,进而削弱整体热集成效果。第三是长周期稳定运行问题。规模化示范不仅需要各类催化剂具有较高初始性能^[264],已有分析认为,PEM

电解在动态工况下会受到膜降解、金属迁移、界面应力和气体交叉等因素影响,从而限制系统寿命和年利用率^[267],因此还需要电解槽、吸收剂、催化剂、压缩机和分离系统在连续运行及启停循环过程中保持稳定、可预测的运行规律。

5 结论

本文系统地回顾了燃煤电厂 CC to e-Fuels 的整个技术链,涵盖了碳捕集、氢气获取、合成气生成与转化、产品分离与精制、政策认证以及经济制约等关键方面。

(1) 燃煤电厂烟气中二氧化碳浓度与超低排放标准,为大规模碳捕集提供了基础;

(2) 对现有燃煤机组而言,燃烧后捕集中的化学吸收法仍是近期最具工程基础的捕集路线;

(3) 碱性电解水 (AWE) 与质子交换膜 (PEMWE) 更适合近期规模化供氢,SOEC 共电解则属于中长期高温耦合方向;

(4) 在转化路线方面,RWGS - FT 和甲醇中间体路线虽然流程较长,但反应边界清楚、工业基础较好,更适合作为近期示范放大的主干路线;

(5) 直接 O₂ 加氢制高碳烃、ICCU 及一体化反应器虽可缩短流程,但仍受 CO₂ 活化、C - C 偶联、产物选择限制;

(6) 系统效率和分离循环仍是工程放大的关键问题;

因而,煤电 CC to e-Fuels 的后续突破重点不宜只关注单元反应效率,更应考虑如何降低绿氢成本、提高目标馏分收率、减少循环分离负荷,并明确生命周期减排核算与燃料认证边界。通过系统协同作用,以稳定、经济的碳源和绿色氢源为基础,通过连续转化、产品分离与减排认证等关键环节,可形成连续化、可放大、可认证且成本可承受的 e-Fuels 制备路径。

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