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生物乙醇制备航空煤油的研究进展 1

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摘 要 生物基航空煤油是一种可持续、绿色环保的航空燃料，能够有效降低航空业的碳排放，具有巨大的应用前景。本文对以生物质为原料制备航空煤油的工艺路线进行了综述，我国生物乙醇产业规模发展快速，产量充足，着重阐述了生物乙醇制备航油的工艺流程，对传统醇制航油技术（Alcohol to Jet Fuels）三个主要反应乙醇脱水制乙烯、烯烃低聚和加氢反应的工艺反应条件和催化剂进行分析总结，并介绍了乙醇碳碳偶联和加氢脱氧制备航空煤油技术，包括制备高碳醇的反应机理和催化剂以及对加氢脱氧反应的研究等，指出乙醇制备航空煤油工艺技术现阶段所面临的成本较高、制备新型催化剂等问题，针对该领域未来的发展方向提出展望，为今后生物乙醇制备航空煤油工业化发展提供参考。

关键词 航空煤油；生物乙醇；催化剂；高碳醇；加氢脱氧

分类号

Research progress on the preparation of aviation kerosene using bioethanol

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ABSTRACT In recent years, the Chinese government has put forward the "dual carbon" goal of achieving carbon peak by 2030 and carbon neutrality by 2060. In order to achieve this goal, the petrochemical industry is facing the urgent challenge of transformation and development, energy conservation and emission reduction. Bio-based aviation kerosene represents a sustainable and environmentally friendly alternative for reducing carbon emissions in the aviation industry, offering significant promise for widespread adoption. This paper provides a comprehensive review of the process for producing aviation kerosene from biomass. Vegetable oil, pyrolysis oil and other oil crops, lignocellulosic, sugar and starch biomass can be used as raw materials for bio-aviation kerosene. The production technology of bio-based aviation kerosene is divided into oil to jet fuel, gas

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to jet fuel, alcohol to jet fuel and sugar to jet fuel. With the rapid development of China's bioethanol industry and abundant production, the energy supply diversification strategy represented by ethanol and other alternative energy sources has become a direction of energy policies in various countries. The use of bioethanol as a raw material for the preparation of aviation kerosene plays an important role in the environment, economy and sustainability. This paper focuses on the process of converting bioethanol into aviation fuel. The paper analyzes and summarizes the reaction conditions and catalysts involved in three main reactions: ethanol dehydration to ethylene, olefin oligomerization, and hydrogenation. At present, ATJ process still has some disadvantages such as long process flow and low conversion efficiency. The route from ethanol to jet kerosene is complex and requires three different catalysts. We need to develop a catalyst that can catalyze both dehydration reaction and oligomerization hydrogenation reaction, improve conversion efficiency and reduce production cost. Additionally, it introduces the carbon-carbon coupling of ethanol and hydrodeoxidation for aviation kerosene production, including discussions on reaction mechanisms and catalysts for high carbon alcohol preparation. In the Guerbet condensation reaction of ethanol, the presence of by-product water will hinder the reaction. Therefore, a catalyst for ethanol aqueous carbon-carbon coupling reaction to produce high-carbon alcohols was proposed. The catalyst with good water resistance can maintain its activity and selectivity in the presence of water, effectively inhibit the interference of water molecules, and thus improve the efficiency and stability of the catalytic reaction. Jet kerosene was obtained by hydrodeoxidation of high carbon alcohols, in which noble metal and molybdenum based catalysts had good catalytic performance. Transition metals combined with Mo2C catalysts can selectively break C-O bonds in polyols and avoid C-C bond breakage. Research and development of efficient hydrodeoxidation catalysts can promote the conversion of high-carbon alcohols to hydrocarbons, which provides important support for the development of alternative aviation fuels. The paper highlights the current challenges facing ethanol-based jet fuel production, such as the high cost of bio-jet fuel preparation, how to reduce its cost, solve preparation challenges, and improve its economy is still the focus of research, and the need for new catalysts in the process. Furthermore, it proposes future development directions in this field, offering valuable insights for the industrialization of bioethanol-based aviation kerosene production.

KEY WORDS aviation kerosene; bioethanol; catalyst; high carbon alcohol；hydrodeoxidation

近年来中国政府提出了 2030 年实现碳达峰、2060 年实现碳中和的“双碳”目标，为了实现这一目标，石化行业面临着转型发展、节能减排的迫切挑战[1]。在碳中和目标的推动下，炼化企业需要以原料构成和加工技术为出发点，积极探索低碳、零碳原料的炼制技术，以实现低碳发展[2]。航空业是高空温室气体排放的主要来源，其中航空煤油是飞机主要的动力来源。生物航油以生物质为原料，可替代部分传统航油，实现减排 55%至 92%，具有显著环保优势[3–5]。生物航空煤油技术路线具有全生命周期温室气体排放降低的潜力，采用生物航空煤油能够有效减少航空业的碳排放，推动航空业可持续发展。

生物质能是一种可再生的优质能源，植物油、热解油等油类作物、木质纤维素、糖和淀粉生物质都可以作为生物航煤的原料[6,7]。近年来，为解决化石能源的短缺和减少碳排放的问题，以生物质为原料制备航空煤油的工艺技术有了长足的发展[8,9]。生物航空煤油的制备工艺技术主要有生物油制航煤技术、生物质经合成气制航煤技术、醇和糖制航煤技术。本文对近年来生物乙醇制备航空煤油工艺技术相关领域的文献进行了整理，重点介绍了以生物乙醇为原料制备航空煤油的发展现状，该技术包括醇脱水、烯烃低聚和烯烃加氢三个主要反应步骤，以及高碳醇加氢脱氧制备航空煤油技术，并对该领域的发展前景进行一定的展望。为生物乙醇制备航空煤油的后续研究提供了重要参考和理论依据。

1 生物基航空煤油概述

航空煤油的主要成分通常包括碳数在 C_8 到 C_{16} 之间的烃类，成分包含烷烃和异构烷烃、环烷烃，以及少量的烯烃和芳香烃[10]。生物基航空煤油是指直接或间接利用生物质合成的航空煤油，其含硫量较低，尾气排放污染小，还有良好的低温流动性和热稳定性[11]。此外，生物基航煤与传统航空煤油在技术上基本兼容，不需要对飞机或基础设施进行显著改动，这也有助于减少对化石燃料的依赖，同时促进可再生资源的利用。 生物基航空煤油的生产涉及的生物质来源可以分为可食用植物作物、非食用油料作物和木质纤维素生物质以及藻类等[6,12,13]。将不同类型的原料转化为生物航空煤油的生产工艺路线众多，各路线的简要流程如图 1 所示[5]。

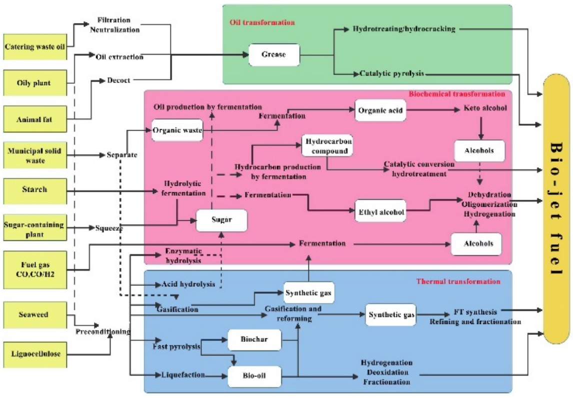

图 1 生物航煤主要制备技术[5]

Fig.1 Main preparation technology of biological aviation kerosene[5]

Wang 等[14] 按照生物航煤生产技术分为油制航煤 (OTJ)、气制航煤 (GTJ)、醇制航煤(ATJ)以及糖制航煤 (STJ) ，如表 1 所示是制备航空煤油主要途径比较。在技术成熟度方面，油制航油目前领先于其他技术，但仍面临诸如原料可得性、温室气体排放和缺乏芳烃等问题需要解决。生物质经合成气制航油路线已有示范工厂运营，但高资本成本仍是其商业化的主要障碍。ATJ 工艺路线是从生物质制取醇转化为航空煤油，可通过工艺强化和研发新型催化剂等方法来改进工艺的高耗能，以补偿醇生产的高成本和低产率[15]。醇制航油路线显示出将生物醇转化为航空燃料的潜力，但需要解决催化升级步骤与醇生产的整合挑战。此外，糖转化为液态烃燃料的水相催化转化在实验室和中试阶段展示出了潜力，但需要进一步改进以提高其经济前景。生物航空煤油生产工艺受到了广泛关注，在航空燃料市场中占据着重要地位，尽管目前存在一些挑战，但从长远来看，生物航空煤油有望逐渐减少对传统石油航空煤油的依赖，并直接作为航空燃料使用。

表 1　生物质制备航空煤油的主要途径[16]

Table 1 The main way of preparing aviation kerosene from biomass[16]

	OTJ	GTJ	ATJ	STJ
Ingredients	Vegetable oil	Lignocellulosic, urban and agricultural residues	Biomass-derived alcohol	Sugar, furan
Reaction step	1. Hydrotreating 2. Fractionation	1.Gasification 2. Fischer-tropsch synthesis 3. Fractionation	1. Dehydration 2. Oligomerization 3. Hydrogenation 4. Fractionation	1. Deoxygenate 2.C-C coupling 3. Hydrogenation 4. Fractionation
Catalyst	It is mainly alumina supported metal sulfide	Fe base and Co base supported catalysts	Heterogeneous and homogeneous acid catalysts	Heterogeneous catalyst
Minimum selling price ($/gal)	4.4-5.1	3.9-4.3	--	>3.5
Greenhouse gas emission (g CO_2/MJ)	13-141	2-10	--	15-49
Aromatic-containing aviation coal	NO	YES	YES	YES
ASTM approved fuel	Yes, mixed with fossil jet fuel up to 50%	Yes, mixed with fossil jet fuel up to 50%	Yes, mixed with fossil jet fuel up to 50%	ASTM test phase

随着国际石油需求的进一步增加和国际油价的上涨，以乙醇等替代能源为代表的能源供应多元化战略已成为各国能源政策的一个方向。生物乙醇是世界上应用最广泛的可再生能源，许多国家和地区正在积极推动生物乙醇产业的发展[17,18]。全球生物乙醇产业正处于从以粮食为主的一代产业向以非粮原料（如秸秆、木薯、枯草）为主的二代产业，甚至向以藻类等为原料的第三代产业的转变期。近年来，全

球燃料乙醇产量发展快速，美国和巴西分别约占全球产量的 54%和 30%。 中国的生物乙醇产业以粮食为原材料的第一代工艺为主，产能占比超过 70%，主要使用玉米和小麦等作物，是第三大乙醇生产国，约占全球的 4%[19-21]。生物乙醇产业在面对人口众多和粮食需求增加的背景下，选择非粮原料作为生产乙醇的方向显得尤为重要，这有助于避免与粮食资源的竞争，并促进生物乙醇产业的可持续发展。但面临多重挑战，高昂的生产成本、非粮原料供应的可持续性和有效的环境保护措施也是亟待解决的关键问题。

因此，用生物乙醇作为制备航空煤油的原料，对环境、经济和可持续性都有重要作用。开发乙醇的高值高端利用技术不仅能够与现行乙醇产业接轨，保障其发展，还有助于我国能源结构的多元化，进而保障国家的能源安全。

2 乙醇制备航空煤油工艺技术

乙醇制航油技术（ATJ）路线，如图 2 所示，涉及三个主要步骤：①乙醇脱水生成相应的烯烃；②烯烃低聚成新的低聚烯烃；③低聚烯烃氢化成饱和烃产物。通过 ATJ 工艺生产的生物航空煤油可以与化石喷气燃料混合使用，其中生物航空煤油的体积百分比高达 50%[22,23]。ATJ 整个工艺流程的所有工艺步骤都已在商业相关规模上得到证明，最大限度的降低了扩大生产规模的风险。下面将从乙醇脱水、烯烃低聚和加氢三个反应对 ATJ 工艺进行综述。

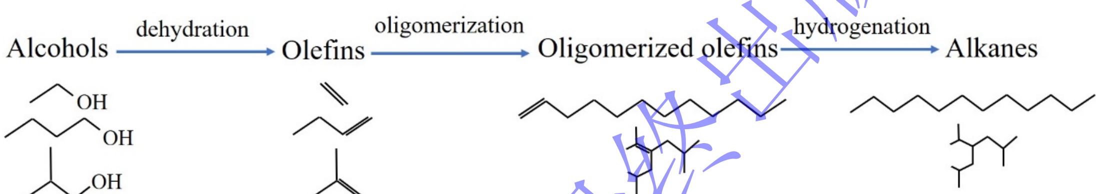

图 2 醇制航油流程图

Fig.2 Flow chart of alcohol jet fuel

2.1 乙醇脱水制烯烃的研究

目前，乙醇脱水制乙烯技术比较成熟，已成为调整能源结构、减少环境污染、促进国民经济和社会可持续发展的重要途径之一。该技术具有产物纯度高、易于提纯、生产工艺简单等优点。针对生物质乙醇脱水制乙烯，当前的研究主要集中在催化剂的开发和工艺优化上，广泛研究的催化剂包括活性氧化铝、沸石、磷酸和磷酸盐等，工业上常用的有 HZSM-5 催化剂、活性炭负载型催化剂和活性氧化铝。然而，生物乙醇主要通过农作物、有机废料发酵经分离提纯得来，浓度约为 13%-26%。目前使用的催化剂对乙醇浓度要求较高对于低浓度乙醇的应用，目前的研究较少，存在催化剂活性不足和稳定性问题，限制了技术的进一步发展。

2.1.1 工艺反应条件的影响

Cheng 等[24]指出乙醇脱水有两种可能的反应机制，分别是有利于乙烯形成的分子内脱水吸热反应和产生乙醚的分子间脱水放热反应。反应温度是影响乙醇催化脱水制备乙烯的重要因素之一，当反应温度在 150 ~ 300 ℃时，主要进行反应（2），乙醇脱水生成乙醚，而当反应温度在 300 ~ 500 ℃时，发生反应（1），生成乙烯。反应温度超过 500℃时，则会发生反应（3），乙醇脱氢生成乙醛，同时，水的生成会导致乙醇的蒸汽重整，发生反应（4）。

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \tag{1}$$

$$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O \tag{2}$$

$$C_2H_5OH \rightarrow C_2H_4O + H_2 \tag{3}$$

$$C_2H_5OH + H_2O \rightarrow 4H_2 + 2CO \tag{4}$$

乙醇的浓度也会对乙醇脱水反应造成影响，乙醇不同浓度下的反应转化率和选择性会有差异[25]。祝阳[26]通过实验使用 4A 分子筛作为反应催化剂，实验表明乙烯转化率随乙醇浓度的变化不大，但选择性随乙

醇浓度变化有明显变化。乙烯选择性的变化可能是由催化剂的不同表面酸性引起的，低浓度乙醇中水的存在作为加热载体，有利于保持反应温度稳定，还能与烯烃中间产物竞争吸附，阻止乙烯的进一步反应，防止催化剂积炭失活，从而提高了选择性。

乙醇质量空速是影响反应进程以及乙烯产量的重要指标。王菊等[27] 通过对乙醇脱水制乙烯工艺实验，发现随空速降低，乙醇的转化率逐渐增加直至平衡。在一定量的催化剂的情况下，活性位点数量有限，在高空速下，不能容纳大量的乙醇和水，会导致乙烯的收率下降[24]。同时，当空速增加时，乙醇分子在催化剂床层的停留时间变短，少部分乙醇还来不及反应即被带出催化剂床层，从而导致转化率降低。

2.1.2 催化剂的影响

乙醇脱水生成乙烯是一个酸催化反应[28]，常见酸性催化剂包括金属氧化物催化剂、磷酸催化剂、分子筛催化剂和杂多酸催化剂，如表 2 是乙醇脱水催化剂性能的比较。Al_2O_3 是最常见的氧化物催化剂，也是酸碱双功能催化剂[29,30]，为提高催化剂的表面积和孔结构，在 Al_2O_3 的基础上，又研发出二元氧化物和多元氧化物催化剂，如 γ- Al_2O_3、MgO- Al_2O_3 等。酸碱双功能催化剂具备较长的使用寿命，稳定性高，能够持续保持其催化活性和选择性，提高反应效率。

表 2 乙醇脱水催化剂的性能的比较

Table 2 Comparison of performance of catalysts for ethanol dehydration

Catalyst	Catalyst preparation method	Reaction temperature	Ethylene yield	Reference
Cu-SSZ-13 zeolite	Cu-tetraethylenepentamine complex was synthesized by one pot method	212℃	＞99%	[31]
WO3/MCF-Si	WO3 was impregnated on MCF-Si carrier by initial wet immersion method	400℃	98.3%	[32]
W/Pd/TiO2	TiO2 negative support was prepared by solvothermal method, and Pd was impregnated first and W was impregnated by equal volume impregnation method	400℃	68.1%	[33]
Ni/Sr-ZSM-5	H-ZSM-5 with Si/Al molar ratio of 25-30 was converted to Sr-ZSM-5 by ion exchange, and then Ni was loaded on Sr-ZSM-5 by impregnation method	250℃	95%	[34]
HT-γ-Al2O3	HT-γ-Al2O3 was synthesized by solvent protection and hydrothermal treatment	450℃	98%	[29]
HPW/Tlb	HPW/Tlb was prepared from phosphotungstic acid hydrate and 1.5mm diameter silicon trilobes	210℃	96%	[35]

目前研究较多的分子筛催化剂是 ZSM-5 分子筛催化剂，ZSM-5 分子筛比表面积高，传质孔道规整并且具备较高的酸性，对于乙醇脱水有高活性。Ouayloul 等[36]通过对 ZSM-5 分子筛的酸性改性的方法，调节催化剂表面酸性，使得乙醇在低温下选择性地脱水生成乙烯。 Zhan 等[37] 研究了 HZSM-5、磷改性 HZSM-5 和镧磷改性 HZSM-5 催化乙醇脱水制乙烯的反应，实验结果表明，镧磷改性 HZSM-5 的催化性能和抗结焦能力最强，其中 0.5%La-2%PHZSM-5 的抗结焦能力最强，如图 3 为 H-ZSM-5 分子筛催化乙醇脱水反应机理图。分子筛催化剂研究和应用的关键是要实现在醇脱水反应中提高稳定性，能够长时间保持催化活性而不发生结构变化或失效，减缓催化剂积碳而导致的失活。杂多酸催化剂是含有氧桥的多核配位物的催化剂，用于乙醇脱水制乙烯的杂多酸催化剂具有反应温度低等优点，但杂多酸催化剂在使用时通常需要负载在载体上，存在损耗严重、制备成本高的问题[38,39]。催化剂在乙醇脱水制乙烯过程中起着重要作用，制备高效且稳定性能好的催化剂是下一步进行的主要工作。

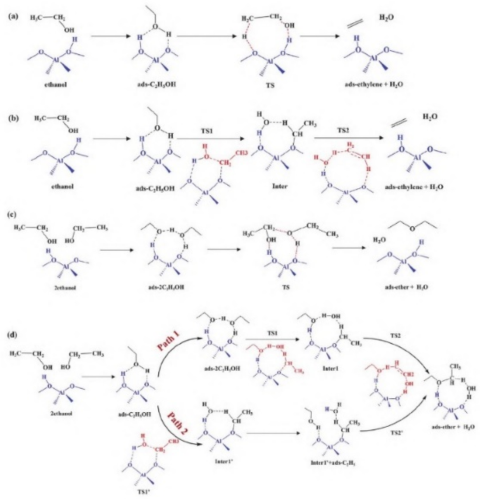

图 3 H-ZSM-5 分子筛催化乙醇脱水反应机理图[40]

(a)生成乙烯的协同反应机理；(b)生成乙烯的分步反应机理；(c)生成乙醚的协同反应机理；(d)生成乙醚的分步反应机理

Fig.3 Diagram of mechanism of ethanol dehydration catalyzed by H-ZSM-5 molecular sieve[40]

(a) the synergistic reaction mechanism of ethylene production; (b) the step-by-step reaction mechanism of ethylene generation; (c) Synergistic reaction mechanism for the formation of ether; (d) Step reaction mechanism of producing ether

2.2 乙烯低聚反应的研究

烯烃聚合是指通过化学反应将烯烃单体聚合成高分子量的聚合物，广泛应用于塑料、橡胶等行业。烯烃聚合技术涵盖了从聚乙烯、聚丙烯到特种聚烯烃等多种聚合物的生产。近年来，烯烃聚合技术取得了显著进展，主要集中在优化催化剂、推广环保技术和开发新型聚合物三个方面。优化催化剂目标在于提高反应效率和产品质量，环保技术则致力于减少环境负担，使用更环保的反应条件和材料。同时，开发具有特殊功能或性能的新型聚合物，如高性能塑料和功能性聚合物，以满足市场对高附加值产品的需求。尽管烯烃聚合技术已有重大进展，仍需解决一些技术挑战，特别是在催化剂固载和替代昂贵助催化剂方面的研究，以进一步推动该领域的发展。

2.1.1 工艺反应条件的影响

反应条件如温度、压力和空速以及催化性能等对乙烯低聚反应都会有影响的。Attanatho 等[41]通过实验制备了片状 Ni-AlSBA-15 催化剂，并在连续流动固定床反应器中在空速（0.56-4.5 h^{-1}）、温度（150-350 ℃）和压力（1-20 bar）的各种条件下进行乙烯低聚实验，最佳反应条件为：反应温度 275-300℃，反应压力 20 bar，空速 0.56 h^{-1}，在此反应条件下，乙烯转化率可达 98- 99mol%。由此可得，在高温、高压和低空速条件下有利于 C_{8+}碳氢化合物的生成。

2.2.2 催化剂的影响

乙醇转化为生物航空燃料需要制备高活性、高稳定性的乙烯低聚催化剂。乙烯低聚催化剂可以分为均相和非均相两种类型。在均相催化剂中，常见的是有机过渡金属配合物，由含有过渡金属的化合物与含有配位能力的有机配体组成[42]。乙烯在催化剂的过渡金属活性位点上发生链增长反应 ，但这类配合物需要通过助催化剂适当比例的激活，才能实现高催化活性和选择性[43]。Bekmukhamedov 等[44]考察了镍基催化剂在乙烯低聚反应中的应用，以及镍中心的电子态和配位态对催化性能的影响。镍基催化剂优点是高活性，产物中不存在聚合物，以及较低的温度（25-30℃）和乙烯压力（10-20 bar）而降低低聚反应的能量成本。Panpian 等[45]制备 NiAlKIT-6 催化剂，通过实验测得乙烯转化率> 95%，C_8+选择性高达 55%，催化剂表现出良好的稳定性。但是，均相催化剂存在回收困难、需大量的助催化剂活化、链长难以控制等缺点。

虽然均相催化体系在乙烯低聚反应中处于中心地位，为解决均相催化剂存在问题，非均相催化剂开始被提出并研发[42,43]。常见的非均相催化剂载体有：硅胶、分子筛和碳纳米管等。轻质烯烃也可以通过

ZSM-5 分子筛催化低聚反应转化为长链烯烃，为生产航空煤油系列产品开辟了一条可持续的途径[46–48]。多相催化体系可以减少使用有机溶剂，易于分离反应介质和催化剂回收，但价格一般比较昂贵。

2.3 烯烃氢化制烷烃的研究

烯烃低聚物首先经过蒸馏分离柴油和航空煤油以及轻质烯烃。在石油化工工业中，加氢饱和是一种常见工艺，用于完成烯烃的氢化反应，氢化过程在固体催化剂上进行，该催化控制反应可在相对高压（>20bar）和高温（200-350℃）条件下完成[49,50]。通过蒸馏分离的轻质烯烃（C_4-C_8）再循环回到低聚步骤，低聚产物在 370℃和空速 $3h^{-1}$ 下加氢，加氢的条件是活性炭上含有 5%重量的钯或铂[14,51]，由氢化步骤产生的 C_8-C_{16} 烷烃适用于可再生航空燃料。过量的氢气被引入反应器中，烯烃经过氢化反应，使双键被饱和，从而确保所有的烯烃都转化为链烷烃。这对于确保燃料的低反应性至关重要，因为饱和的产物通常比烯烃更加稳定，有助于提高燃料的质量和性能。

3 乙醇碳碳偶联和加氢脱氧制备航空煤油工艺技术

3.1 制备高碳醇的研究

3.1.1 Guerbet 反应机理及其催化剂

生物乙醇作为制备高碳醇的原料，低碳醇乙醇通过 Guerbet 反应生成高碳醇。乙醇 Guerbet 反应有直接缩合和间接缩合两种反应机理，Guerbet 直接缩合反应是通过活化乙醇 β 位 C-H 键，与另一分子乙醇羟基脱水生成正丁醇；间接缩合反应是通过乙醇脱氢成乙醛，然后羟醛缩合成丁烯醛，最后氢化为饱和醇[52,53]，图 4 是乙醇间接缩合反应原理图。

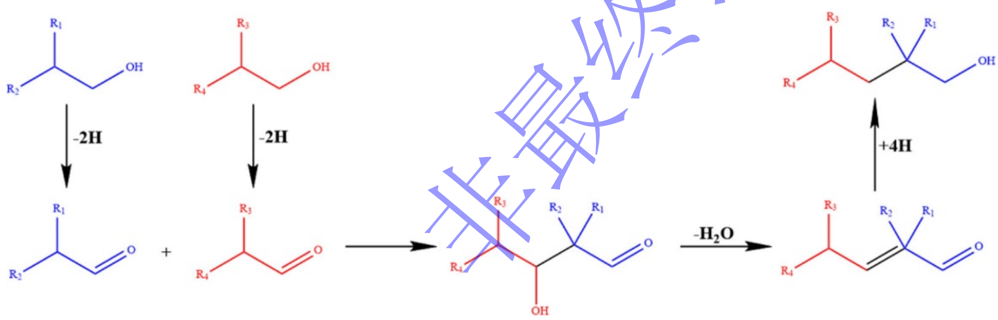

图 4 乙醇间接缩合反应原理图[54]

Fig.4 Schematic diagram of indirect condensation reaction of ethanol[54]

生物航空煤油的制备过程中，首先需要制取 $C_{8\text{-}16}$ 醇，而实现高收率和高选择性的长链高碳醇，特别 C_{8+}醇的合成仍然是一个巨大的挑战[55]。Guerbet 偶联反应提高 C_{8+}高级醇的产率，促进二次改质以延长碳链，同时具有水热稳定性和碱性位点的催化剂是关键。生物乙醇制备高碳醇的催化剂包括有金属氧化物、羟基磷灰石（HAP）和负载型金属催化剂，其中负载型金属催化剂对反应催化有较好的性能[56]，如表 3 是制备高碳醇催化剂的比较。负载型过渡金属催化剂如：Pb、Cu、Ni 基催化剂等，可显著地促进乙醇的偶联反应和提高高碳醇的选择性，通过调整酸碱性，促进乙醇脱氢和乙醛的羟醛缩合[57–59]。对于非负载型催化剂，反应条件相对严格，而且高碳醇选择性不高，即使温度升高，提高高碳醇选择性的效果有限，因为这可能导致大量气体副产物的生成。因此，为了改善催化效果和提升催化剂的活性，通常以过渡金属负载在载体上，作为乙醇转化为高碳醇的催化剂。

表 3 制备高碳醇催化剂的比较

Table 3 Comparison of catalysts for preparation of high carbon alcohols

Catalyst type	Catalyst	Catalyst application characteristics	Reference
Unsupported	Hydroxyapatite	Different preparation methods of HAP (ultrasonic, microwave and autoclave) can affect the catalytic activity of ethanol conversion. The number and strength of alkaline sites on the surface of hydroxyapatite are mainly affected by the use of ultrasonic wave and microwave. In this catalytic system, the conversion rate and product selectivity can be adjusted by changing the surface distribution of acidic and alkaline sites, and the difference in Ca/P ratio on the surface of hydroxyapatite solids leads to different catalytic activities of hydroxyapatite in ethanol conversion.	[60]

catalyst	Hydrotalcite	Compared with a single MgO catalyst, MgO mixed oxide has a higher catalytic activity. Mgo only has a strong basic site and cannot generate n-butanol and C_{4+} products, resulting in a very low activity for ethanol dehydrogenation. Lewis acidic site is required to stabilize acetaldehyde intermediates during the reaction. The adjacent Lewis acid-base sites on Mg-Al mixed oxide catalysts can promote the synthesis of C_{4+} compounds.	[61,62]
	CaC_2	Calcium carbide (CaC_2) has excellent catalytic activity in the formation of C_4-C_9 alcohols by ethanol condensation at 275~300℃. The alkyne group in CaC_2 plays an important role in the catalytic pathway and has a strong hydrogen absorption capacity.	[63]
Supported catalyst	Single metal supported catalyst	Ni, Cu, Ag and PD-based catalysts, supported metal catalysts can decrease the reaction temperature and increase the selectivity of high carbon alcohols due to their dehydrogenation performance and adjustable distribution of active sites. Metals are responsible for ethanol dehydrogenation and hydrogenation of unsaturated aldehydes while the adjacent Lewis acid base provides the active center for acetaldehyde condensation and subsequent dehydration.	[56,64]
	Multi-metal supported catalyst	The introduction of Ni-Co bimetallic catalysts, Sn-Ni/CS catalysts and other polymetallic catalysts significantly improved the dehydrogenation efficiency of ethanol, although there were some limitations in the catalytic process. The increase of metal loading can improve the conversion of ethanol, but it is also accompanied by the formation of a large number of by-products such as gas and alkane. In contrast, reducing the load is beneficial to increase the selectivity of high-carbon alcohols, but this may affect the conversion rate.	[65]

3.1.2 水对 Guerbet 反应的影响

在乙醇的 Guerbet 缩合反应中，副产物水的存在会对反应的进行造成阻碍。此外，水还会对催化剂表面的酸碱位点产生影响，导致催化剂的催化性能降低[54,66]。Hanspal 等[67]通过乙醇 Guerbet 缩合反应进行研究发现，当进料加入水后对丁醇的产生有明显的抑制作用；而从反应器的进料中去除水后，丁醇和乙醛的产生速率恢复到原始稳态值的 70%以上，表明水与催化剂 HAP 表面之间存在可逆的相互作用。水的存在改变了丁醇形成的平衡，竞争性吸附在催化活性位点上。水与 HAP 表面上的磷酸根基团的相互作用以及水对丁醇形成的抑制作用表明，磷酸根基团可能影响到 C-C 键形成的活性位点。

生物乙醇通常以水溶液形式存在，所以在水中直接转化生物醇将具有很大优势[68,69]。Liao 等[70]课题组研发出生物乙醇碳碳偶联和重质醇加氢脱氧集成催化工艺制备生物航空煤油碳氢化合物的新途径。以 Na/Ni@C 为催化剂，在水溶液中直接完成了生物乙醇的碳碳偶联反应，C_8-C_{16} 产物的选择性达到 67.1%。刘文平[71]制备了非贵金属 Sn 改性的 Ni 基催化剂，在 250 ℃的水相环境下，Ni/Sn 比为 20 的 NiSnH 催化剂催化乙醇水相碳碳偶联反应生成混合高碳醇，C_{4+}高碳醇在液相产物中选择性高达 91.6%。生物乙醇碳碳偶联反应，有良好耐水性的催化剂能够在水存在的环境下保持其活性和选择性，有效地抑制水分子的干扰，从而提高催化反应的效率和稳定性。

3.2 高碳醇加氢脱氧反应的研究

与生物乙醇相比，高碳醇具有更高的十六烷值、更高的能量密度、更好的共混稳定性和压缩点火质量等，这归因于高碳醇分子的碳链更长，高碳醇无论物理性质还是燃烧性能都与运输燃料更相容，更适合作为航空燃料使用，能够提供更高的航程和能量输出[72–74]。高碳醇可以通过加氢脱氧反应得到烃类航空煤油，加氢脱氧反应的关键是选择性地断裂多元醇中的 C-O 键并避免 C-C 键断裂[75]。贵金属和钼基催化剂因其出色的加氢脱氧（HDO）活性而备受关注。

其中 Mo_2C 表面具有高的氧结合能，在高碳醇加氢脱氧反应中有良好的催化性能，并具有水稳定性和抗焦炭性能。此外，金属和 Mo_2C 之间的强金属和负载相互作用也可以调节加氢活性和特定选择性[76,77]，用过渡金属对 Mo_2C 表面进行部分修饰可以产生不同的活性位点来控制 HDO 反应途径，即选择性 C-O 键断裂，但 Ru、Pt、Pd 在高碳醇的加氢脱氧反应中具有较强的 C-C 键断裂活性，不利于高碳烃的生成。

钟全旺等[78]　对 2-乙基-1-己醇进行加氢脱氧反应，使用引入过渡金属 Co 的 Mo_2C 催化剂，与未掺杂的 Mo_2C 相比，添加 2%的 Co 后，虽然转化率降至 80.9%，但 3-甲基庚烷的选择性提高至 94.3%。如图 5 所示，选取了不同分子结构类型的典型高碳醇作为原料进行加氢脱氧实验，碳骨架保留率超过了 87%，因此上述实验结果表明，2% Co-Mo2C 对不同碳链分子构型的高碳醇都具有良好的加氢脱氧活性和碳骨架

保留能力。加氢脱氧反应的催化剂对于高碳醇的转化至烃类是非常重要的，在工艺中维持高碳醇的支化碳骨架，并且实现选择性地断裂 C-O 键。研究和发展高效的加氢脱氧催化剂可以推动高碳醇向烃类的转化，并为替代航空燃料的开发提供重要支持。

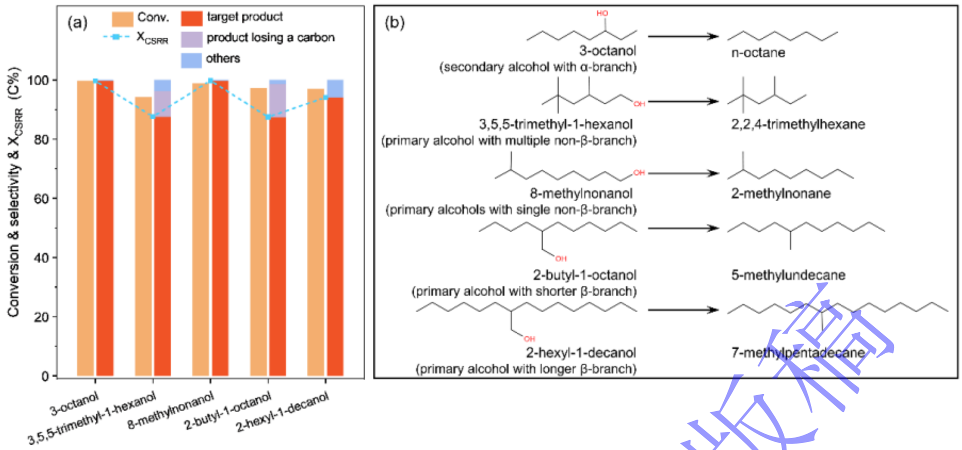

图 5 (a)不同分子构型的高碳醇在 2% Co-Mo2C 催化剂上的加氢脱氧反应活性。(b)碳骨架保留的加氢脱氧反应示意图[78]

Fig.5 (a) Hydrodeoxygenation activity of high-carbon alcohols with different molecular configurations on 2% Co-Mo2C catalyst. (b) Schematic diagram of hydrodeoxidation reaction with carbon skeleton retention[78]

4 结语

本文介绍了以生物乙醇为原料制备航空煤油的两种工艺路线， ATJ 技术和高碳醇加氢脱氧工艺技术。可持续航空燃料现在已经成为航空业减少碳排放和减少其整体环境影响的重要措施，尽管替代航空生物燃料的需求正在迅速增长，但在替代化石航空燃料之前，仍有许多挑战需要克服，根据本文的综述内容，提出几点建议与展望。

（1）当前研究重点在于将生物质转化为生物航空煤油，以生产可再生的航空煤油。关注点主要集中在可再生资源的利用、较低的温室气体排放、可持续性以及成本可承受性。生物航油制备成本高昂，如何降低其成本、解决制备难题，并提高其经济性仍然是研究的重点，尤其是通过生物乙醇制备生物航空煤油的路线，虽然生产的航空煤油已经用于商业飞行，但成本较高且大规模生产还有一定的困难。

（2）ATJ 工艺分离每个步骤的产物使得该过程非常复杂和昂贵，还存在产品异构体比例难以控制、工艺流程长、转化效率低等缺点。醇到航空煤油路线复杂，需要三种不同的催化剂，需要我们开发出一种既能催化脱水反应又能催化低聚加氢反应的催化剂，探索新型催化剂结构和生物质预处理方式来提高产率。

（3）生物乙醇发酵液中含有大量的水分，直接对含水乙醇进行提质可以简化昂贵的分离过程。催化生物乙醇升级为高碳醇越来越受到广泛关注，研究一种兼具脱氢、氢化以及羟醛缩合作用的多功能非贵金属催化剂，在保持优异脱氢能力的同时，减弱了对 C-C 键的断裂能力，增强了催化剂自身促进羟醛缩合的能力，从而提高了高碳醇的选择性，这对未来产业化生产高碳醇有十分重要的意义。

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