

载冷剂的流动特性及在水产品贮运 保鲜中的应用研究进展

Research progress on the flow characteristics of secondary refrigerants and application progress in aquatic products storage and preservation system

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摘要:载冷剂是一种传递冷量的中间媒介,利用载冷剂可以提高冷冻效率。文章介绍了载冷剂的分类和特征,主要对载冷剂的流动特性进行了论述,讨论了载冷剂流动过程中的表观黏度变化和流动阻力特性。此外,还论述了不同类型载冷剂在水产品贮运保鲜系统中的应用,其中非相变载冷剂主要应用于食品浸渍冻结,水产品贮藏运输环节中的冷库和冷藏车主要应用了相变材料载冷剂,并对载冷剂未来的发展方向进行了展望。

关键词:载冷剂;流动特性;水产品;贮藏;保鲜

Abstract: The secondary refrigerant is an intermediate medium for transferring cold capacity, which can improved refrigeration efficiency. In this paper, the classification and characteristics of secondary refrigerants are introduced, and discusses the flow characteristics of secondary refrigerants and the apparent viscosity changes and flow resistance characteristics during the flow of secondary refrigerants. In addition, the application of different types of secondary refrigerants in aquatic product preservation and storage system is also discussed, among which non-phase change secondary refrigerant is mainly used in food

impregnation and freezing. The phase change material refrigerant is mainly used in cold storage and refrigerating truck of aquatic product storage and transportation, and the future development direction of secondary refrigerant is prospected.

Keywords: secondary refrigerant; multiphase flow; aquatic products; store; keep fresh

随着“环保”“安全”“节能”三大理念深入人心,以及《联合国气候框架公约基加利修正案》^[1]等相关条例的发布,环保性、安全性、节能性更高的载冷剂备受关注。在此背景下,间接制冷是一种比较理想的制冷替代方法^[2]。间接制冷的关键在于载冷剂,载冷剂作为传递冷量的媒介被用于供冷系统。冷量存储是缓解能源供需差距的有效途径,载冷剂被应用于食品加工、贮藏、运输配送等低温冷链的各环节,具有节能潜力^[3]。在贮运过程中,因外界微生物或自身含有的酶会导致水产品腐败变质,因此利用载冷剂冷冻技术保鲜相当重要。食品类冷冻运输贮藏所选用的载冷剂要求无毒无害、不易发生泄漏,除了要求安全性和节能性外,载冷剂实际应用还需要具备良好的流动特性和换热性能。

文章拟对载冷剂进行详细分类,介绍载冷剂流动过程中的表观黏度变化和阻力特性,并系统阐述其在应用过程中存在的优缺点。在此基础上,系统综述载冷剂在水产品贮运保鲜中的应用进展,主要体现在直接浸渍冻

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结的非相变载冷剂和间接供冷系统中的相变载冷剂的研究进展,旨在为载冷剂用于水产品保鲜贮藏提供参考。

1 载冷剂的种类及特征

载冷剂是一种传递冷量的流体,通常被称为二次制冷剂或传热流体,是单一液体或者由多种物质组成的混合物^[4],载冷剂按其主要成分、原料组成、使用过程是否发生相变可分为不同类型(见图 1)。

1.1 载冷剂的主要类型

1.1.1 根据主要成分分类 根据主要成分,载冷剂可分为盐类、醇类、糖类的水溶液等。盐类水溶液中的盐有氯化钠、氯化钙和氯化镁等,被广泛应用于海洋船舶水产品

的冻结和保存^[5],与空气冻结相比,冷盐水溶液冻结的能耗可降低 25% 以上,其传热速率远高于空气冻结^[6]。而醇类水溶液主要是甲醇、乙醇、乙二醇、丙二醇、丙三醇和醇类的衍生物,醇类作为载冷剂可明显提高冷冻速率,延缓蛋白变性,保持冷冻产品的质量^[7]。但在低温下,丙二醇和丙三醇水溶液的黏度激增,若浓度过高会影响系统运行,实际应用中常见的醇类载冷剂为乙醇水溶液。糖类水溶液载冷剂包括果糖、蔗糖、葡萄糖和转化糖,若将其单独使用,会存在黏度较大、冻结点较高的问题^[8],故常以复配的形式加入到载冷剂中,对水产品冻藏品质起到增效作用。

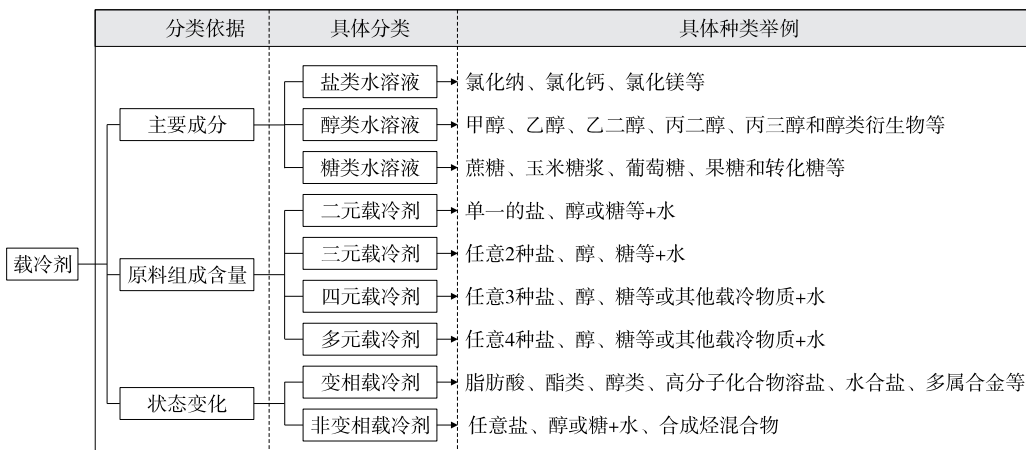


图 1 载冷剂的不同分类

Figure 1 Classifications of secondary refrigerant

1.1.2 根据原料组成分类 由于单一的盐、醇及糖类作为载冷剂大多存在腐蚀性强、挥发性快和黏度大等问题,将载冷剂进行复配可以得到性能更优的多元载冷剂。从原料组成可以分为二元、三元、四元复配载冷剂。常见的二元载冷剂有氯化钙、氯化钠水溶液、乙醇水溶液,食品在氯化钙水溶液中浸渍完会呈苦味,故常包装后进行冷冻;氯化钠水溶液可用于大多数水产品;残留的乙醇会在贮藏过程中挥发掉,故也用于多数食品冷冻保存。常见的三元载冷剂有氯化钠、水与糖类或其他盐类的混合溶液^[9]。辛美丽^[10]提出了一种由乙醇、丙二醇与水组成的三元载冷剂,可用于-30℃的冻结。四元载冷剂大多以盐类、醇类和水为基础,再加入其他新成分或将不同盐类、醇类与水进行复配。马晓斌等^[11]优化了载冷剂配方,其主要组成为乙醇、丙二醇、氯化钠水溶液和甜菜碱,冰点可达-66.10℃,可降低脆肉鲩肌原纤维蛋白的变性。曾庆孝等^[12]将不同比例的乙醇、丙二醇和氯化钠混合组成四元载冷剂,具有冻结点低、热传递性较强、扩散性较低等特点。多元复配载冷剂的冻结点、黏度等物理特性均优于盐类的水溶液、醇类的水溶液和糖类的水溶液载冷剂。

1.1.3 根据使用过程中状态的变化分类 根据使用过程中状态的变化,载冷剂可以分为非相变载冷剂和相变载冷剂。常见的非相变载冷剂有 NaCl 水溶液、CaCl₂ 水溶液、乙二醇水溶液、丙二醇水溶液、丙三醇水溶液、二乙苯混合物、合成烃混合物等^[13];常见的相变载冷剂由有机材料或无机材料组成。相变材料(PCM)在特定温度范围内利用相变潜热,并在物质状态发生变化时吸收或释放大量热量进行能量储存。有机相变材料主要包括脂肪酸、酯类、醇类、高分子化合物等单一或多种组分;无机相变材料主要包括水、熔盐、水合盐、金属合金等单一或多种组分,而低温领域使用的相变材料多为水和水合盐^[14]。一般相变载冷剂的流动特性优于非相变载冷剂,相变材料载冷剂是载冷剂研究的主要目标^[15-16]。

1.2 载冷剂的特征

理想的载冷剂一般具有以下特征:① 低温双向宽温域,可以根据实际需要的温度来复配,使用范围为-75~240℃^[17];② 黏度小,导热系数大,传热效率高。常温下空气的导热系数为 0.026 7 W/(m·K),而大多数液体的导热系数是空气的 4~23 倍^[18];③ 安全无毒,不燃不爆,

腐蚀性小^[19],保证实际应用中的安全性;④ 价钱低廉,原料易得。载冷剂冻结的成本是机械制冷成本的 1/4^[20]。

但实际情况下,载冷剂并不具备所有良好性能。对于常用的载冷剂,不同类型载冷剂的优缺点见表 1。单一组分的盐类和醇类是最常见的载冷剂,因其具有制备快捷、

安全无毒、温域宽等优点常被用于水产品预冷环节^[36]。针对单一组分载冷剂会渗透到食品内部影响品质、腐蚀性较大等,复配了多组分多元载冷剂。但随着组分的增加,冻结点降低却使黏度变大。而相变载冷剂解决了低温下黏度激增的问题,但存在易分层不稳定等技术难题。

表 1 不同载冷剂的优缺点

Table 1 Advantages and disadvantages of different secondary refrigerants

分类依据	种类	优点	缺点	参考文献
主要成分	水	黏度小、比热容大、稳定、安全无毒、价格低廉,传热性能良好	冰点较高,只能满足 0℃ 以上的制冷需求	[21]
	盐类	黏度小、冰点较低、安全无毒、价格低廉	腐蚀性较大,冰点受组分浓度影响较大	[22—24]
	醇类	冰点低、价格低,不易在食品表面残留	低温下黏度激增,有一定可燃性,使用周期短	[8]
	糖类	无色无味,冰点在 0℃ 以下,可满足低温需求,具有较为优良的传热性能	黏度大,用于浸渍冻结时会渗透到食品内部	[25—26]
原料组成	二元	黏度较低,原料易得,制备成本低	可以达到的冰点高,使用范围小	[27—28]
	三元	可以限制溶液渗透到食品中	多一种组分后,黏度变大,腐蚀性相对较大	[29]
	四元	可以达到温域宽	成本相对较高,可行的添加剂较少	[30]
	多元	控制了低温下的黏度激增	制备工艺过程相对复杂	[31]
状态变化	相变	有优异的传热特性,导热系数高、蒸发潜热大,降低装置和运行的费用	存在技术难题,价格昂贵	[32—33]
	非相变	黏度低、比热容大、传热效率高、性质稳定、不易燃易爆、低腐蚀性	蓄冷效果相对较差	[34—35]

2 载冷剂使用过程中的流动特性

2.1 载冷剂表观黏度

载冷剂具有流动性,能够经过管道进行远距离运输,载冷剂的流动特性及输送规律变化是研究的重点。表观黏度是载冷剂流动运输过程中的核心参数。非相变载冷剂的表现黏度受组分含量的影响,韩光赫等^[37]发现溶液组成和温度对以乙醇、丙二醇、氯化钠和水组成的四元载冷剂的表现黏度影响显著。其中氯化钠浓度对体系黏度的影响最大,且温度与黏度呈负相关,当组分总含量一致时,氯化钠含量为 12% 的表现黏度比氯化钠含量为 4% 的大 5.35 mPa·s。

相变载冷剂运输过程中表现黏度的变化比非相变载冷剂的复杂得多。冰浆和水合物浆属于相变载冷剂,由于固液两相流动特性的差异,流动过程中会出现分层现象。不同种类的载冷剂,其表现黏度和在管道中的流变性质存在差异,这也是相变流载冷剂流动特性的重点。Frei 等^[38]提出用宾汉姆模型来描述冰浆的流动特性,冰浆的平均黏度可以按文献^[39]中的公式计算得出。Darbouret 等^[40]研究了层流状态下管道中四丁基溴化铵水合物(TBAB)颗粒体系中浆体的流动特性,并得到 TBAB 水合物浆液黏度与管道直径和流量的预测模型。Qin 等^[41]研究了甲烷水合物浆的流动特性,添加水合物

浆含水系统中,体系黏度增加了 20~60 倍。

2.2 载冷剂流动阻力特性

载冷剂的流动阻力特性是输送过程中的另一个重要参数。对于非相变载冷剂,乙二醇工质黏度、密度、热导率等性质随温度变化,其沿程阻力损失很难确定,针对这一问题,韩立超^[42]提出了乙二醇载冷剂在制冷系统中的水力参数值,为工程实际计算提供了参考依据。颗粒的密度、尺度、浆体的浓度、流速以及浆体黏度等对浆体阻力有重要影响,与白晓宁等^[43]的研究结果一致。郑志等^[44]对管道内载冷剂流动阻力特性进行了研究,提出了湍流时沿程摩阻系数和摩阻的计算方法。关于相变载冷剂流动特性归纳结果见表 2。对于载冷剂的管内流动特性,研究变量通常选取载冷剂种类、流速、管型以及是否需要考虑重力等。通过实操试验、数值计算、仿真模拟等手段,进一步研究载冷剂在管道中的流动特性,基本能满足实际工程中设计的要求^[58]。

3 载冷剂在水产品贮运保鲜中的应用

载冷剂可用于换热器内部间接冷却或直接接触冷却,因其具有蓄冷量大、冷却时间长、可循环利用等优点。载冷剂在水产品预冷、加工和运输环节中被广泛应用,如图 2 所示。载冷剂的应用优势在于,它可以将制冷系统在较小范围内产生的冷量通过管道运输至冷却设备。此

表 2 相变载冷剂的流动特性

Table 2 Flow characteristics of phase change secondary refrigerants

载冷剂	管道类型	研究结果	参考文献
6.5%乙二醇	竖直管	冰粒子的流场和浓度场受到冰浆浓度和壁面温度的影响	[45]
6.5%乙二醇冰浆	水平道	基于多相流动力学提出了一种分析压降模型,以量化冰浆流各相的压降	[46]
冰浆	水平管	建立了一种 CFD-PBM 方法,用于模拟水平管道中的冰浆流	[47]
冰浆	水平管	研究了冰浆在冷却过程中的流动特性,冰浆的凝固特性取决于流速和 IPF	[48]
5%~20%的乙醇	90°弯管	弯管压降受冰浆流速、浓度及弯管曲率影响,冰浆在弯管内流动形成二次流现象	[49]
冰浆	T 型管	冰浆单位压降受流速和含冰率的影响	[50]
TBAB 水合浆物	复杂管道	流速对 TBAB 浆体流动中阻力的影响最大,低浓度 TBAB 浆体在某些工况下表现出了剪切稀化	[51]
天然气水合浆物	长直管	建立了计算水合物浆流动时管输摩阻的数学模型	[52]
16%乙二醇	翅片式换热管	冰浆 HVAC 系统使系统降温速率增加了 7.4%	[53]
THF 水合浆物	直管	研究了水合物浆发生冰堵的颗粒体积分,并得到了 THF 水合物浆的压降系数	[54]
固液两相流载冷剂	直管	提出了载冷剂的压降及流型预测模型,根据模型可准确判断水合物浆的悬浮流动状态	[55]
R11 水合物浆	复杂管道	测定管道中的压降及不同体积分数的载冷剂在不同流速下管道中压力变化	[56]
甲烷水合物浆	回路管道	基于 Herschel-Bulkley 型方程,给出一种预测不同水合物浆流速下的压降和管道摩擦系数的模型	[57]

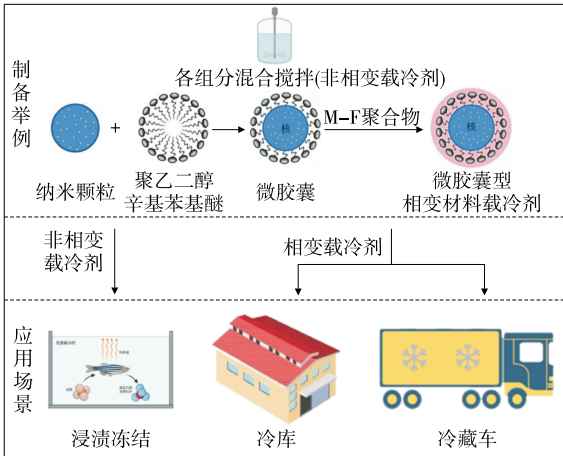


图 2 载冷剂的制备及应用场景^[59]

Figure 2 Preparation and application scenarios of secondary refrigerant

外,载冷剂的使用可减少制冷剂使用量,减少制冷剂的扩散,降低使用过程中的危险。

3.1 非相变载冷剂的应用

冷冻是保持水产品品质的关键一环,以低温载冷剂作为冻结介质的冷冻方式为浸渍冻结,其主要利用二元、三元及多元等非相变类载冷剂作为冷媒,与食品直接或间接接触换热,实现食品快速冷冻^[60]。浸渍冻结时由于物质交换过程中冷冻速率显著提高,形成了细小而均匀

的冰晶,减少了对肌肉组织的损伤,常用于鱼类、虾类、贝类和蟹类等水产品冷加工中,其中在鱼类的液体冷冻处理中应用最为广泛,各类水产品的应用见表 3。张涛^[72]研究发现,采用载冷剂冷冻石斑鱼能维持鱼肉的新鲜度,延长了流通货架期,物流时间可达到 80 h,该时间下其 TVB-N 值为 26.88 mg/100 g, K 值为 47.965%。Liu 等^[64]研究了载冷剂处理乌鳢块的品质变化,结果表明载冷剂冻结比空气冻结能够更好地保持冻藏过程中乌鳢块的品质,其中在-40℃载冷剂中冷冻的样品形成的冰晶平均截面积仅有 86.5 μm²。林婉玲等^[67]将甜菜碱、丙二醇、氯化钠、甘氨酸和甘露醇按照不同比例复配成载冷剂,冷冻处理后的虾品质和感官指标均优于空气冻结的。以-35℃的载冷剂冷冻牡蛎后,牡蛎肉体内几乎无汁液流失,牡蛎肉自身的弹性维持原貌^[70]。以无水乙醇为载冷剂冷冻梭子蟹后,梭子蟹的肌肉品质变化受到温度的影响,温度越低,冷冻品质变化越慢^[71]。总体而言,利用载冷剂冻结水产品有效提高了冷冻速率,减少了冷冻贮藏后水产品的水分流失,延缓了水产品的腐败变质,更有利于水产品贮运保鲜过程中的品质保持。

3.2 相变载冷剂的应用

相变载冷剂具有更高的蓄冷量,主要应用于水产品的冷藏运输和冷冻贮藏环节,通过冷链物流的冷藏车和间接制冷冷库实现。间接制冷系统由载冷剂控制系统回路、制冷剂控制系统回路和相关表盘组成。在载冷剂控

表 3 载冷剂在水产品中的应用举例

Table 3 Examples of the application of secondary refrigerants in aquatic products

水产品种类	应用对象	载冷剂成分	研究内容	参考文献
鱼类	石斑鱼	柠檬酸、丙二醇、低聚糖类和水	载冷剂处理对石斑鱼在常温物流过程中的品质和货架期的影响	[61]
	大黄鱼	自制载冷剂	载冷剂冷冻后大黄鱼贮藏期间品质变化	[62]
	竹荚鱼	20%氯化钙、8%丙二醇、5%海藻糖和水	浸渍冻结与其他冻结方式对竹荚鱼品质的影响	[63]
	乌鳢块	95%乙醇、乙二醇、氯化钠和水	载冷剂冷冻乌鳢块冻藏过程中的品质变化	[64]
	草鱼	自制载冷剂	草鱼冷冻贮藏期间持水能力、冰晶及水迁移规律	[65]
虾类	南美白对虾	自制载冷剂	浸渍冻结与其他冻结方式对南美白对虾品质的影响	[66]
	凡纳滨对虾	甜菜碱、丙二醇、氯化钠、甘氨酸和甘露醇	浸渍冻结对凡纳滨对虾冻藏过程中品质的影响	[67]
	南极磷虾	27% CaCl ₂ 水溶液	冻结方式对南极磷虾品质的影响	[68]
贝类和蟹类	牡蛎	自制载冷剂	浸渍冻结与其他冻结方式对牡蛎品质的影响	[69]
	牡蛎	-35℃低温载冷剂	液浸速冻对牡蛎水分迁移及品质的影响	[70]
	梭子蟹	无水乙醇	低温液体速冻梭子蟹冻藏期间肌肉生化特性的影响	[71]

制系统回路中,载冷剂保存在储液箱内,由水泵运输到换热器中,在换热器中被来自压缩机的制冷剂冷却后,进入冷风机与空气换热释放冷量,最后流到储液箱中,实现载冷剂回路循环。在制冷剂回路中,制冷剂在压缩机内压缩、冷凝后进入换热器,在换热器内与载冷剂交换热量,而后回到压缩机内完成制冷回路循环^[73]。图3为间接制冷系统原理图。

水产品运输过程中若采用传统的块冰、片冰和碎冰进行冷却,会对鱼体造成伤害且鱼体新鲜度相对降低^[74]。此外,无水活鱼运输、低温保鲜、超低温保鲜等水产品保鲜技术需要精确的控温技术。然而,精确的温度控制设备往往成本高昂。随着间接制冷系统的推广,作为冷媒的载冷剂应用越来越广泛,其中相变材料类载冷剂使用最为广泛。班超方等^[75]研制了一种相变温度为-23℃且相变潜热在200 kJ/kg以上可用于冷库的低温复合相变材料载冷剂,符合低温冷库的日常使用。

在冷链物流系统中,将PCM集成到冷藏车的车壁中,通过车壁和环境空气进行热交换来达到降温目的。

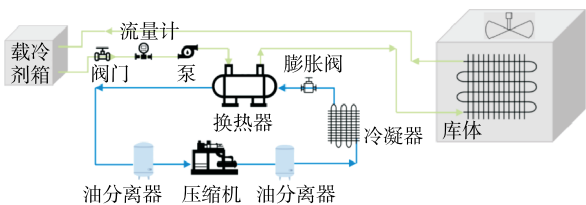


图 3 间接制冷工作原理图
Figure 3 Working principle of indirect refrigeration cold storage

章学来等^[76]开发了一种适用于工作温度为5~15℃的相变储能载冷剂,可用于食品的冷链运输保鲜。还有一种相变温度为4.2℃,相变潜热为247.1 kJ/kg,导热系数为0.965 7 W/(m·K),可用于冷链物流的复合相变材料载冷剂^[77],满足冷藏车低温运输过程中的需求。

4 结论与展望

文章综述了载冷剂的分类及对应的特征,讨论了流动特性研究概况,并总结了应用于水产品冷冻运输贮藏环节的进展。后续研究方向有:① 解决载冷剂具有腐蚀性的问题,若解决这个问题可降低应用实践中的设备管道维护成本,且设备使用过程中的安全性将大大提高;② 应用新型相变材料降低载冷剂在低温下的黏度,低黏度的载冷剂可以降低能耗,从而提高泵送效率;③ 引入仿真模拟计算,仿真模拟强大的计算功能可以模拟载冷剂在各种环境条件下的运行方式和效果,为新型载冷剂的研发提供思路。

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