绿色生物燃料生物丁醇分离新技术

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摘要: 随着石油资源的日益减少，生物丁醇作为一种以生物质为原料的高能量生物燃料，比生物乙醇有着更好的应用前景，是石油等化石能源的首选替代品。然而发酵液中除了丁醇外，还含有丙酮、乙醇以及绝大部分的水，分离效果差及分离成本高成为生物丁醇发展的瓶颈，为此，开发高效节能的分离技术成为生物丁醇能否产业化的关键。传统的提纯方法使发酵液先经过粗分离塔蒸馏，去掉发酵固体物和部分水，得到浓缩的有机溶剂。然后继续用蒸馏法分离物料得到乙醇、丙酮和正丁醇。针对生物丁醇发酵液体系分离困难且能耗大的问题，介绍了吸附、气提、薄膜渗透汽化、薄膜萃取等新型分离技术，尤其重点介绍盐析过程改善了发酵法生产正丁醇的传统精馏工段。通过盐析工艺除去发酵液中大部分的水分，能够极大的降低后续精馏操作的能量消耗，提供一种新的高效、节能分离方法。这些盐析剂廉价易得，容易回收循环利用，并且所使用的无机盐不会污染环境。盐析工艺适用条件温和，操作简单，不仅能节约能耗，同时能够降低 CO_2 排放，实现节能减排。

关键词: 生物丁醇; 分离; 盐析; 萃取

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Emerging Separation Techniques for Butanol Biofuel

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Abstract: Biobutanol, a high-energy biofuel made from biomass, has better application prospects than bioethanol. With the dwindling of petroleum resources, biobutanol is one of the preferred alternatives to petroleum and other fossil energy sources. However, in addition to butanol, the biobutanol fermentation broth contains acetone, ethanol and most of the water. Poor separation effect and high separation cost have become one of the bottlenecks for the development of biobutanol. Therefore, the development of efficient and energy-saving separation technology is one of the keys to the industrialization of biobutanol. The traditional purification method has the fermentation broth first distilled in a prefractionator to remove the fermentation solids and some of the water, resulting in a concentrated organic solvent. The solvent is then separated by distillation to obtain ethanol, acetone and n-butanol. Aiming at the problem of difficult and energy-consuming separation of biobutanol fermentation broth, we introduce emerging separation techniques such as adsorption, gas extraction, pervaporation, and pertraction. Particular emphasis is placed on the salting-out process which improves the traditional distillation section of biobutanol production. Removing most of the water in the fermentation broth through the salting-out process can greatly reduce the energy consumption of subsequent distillation operations, providing a new efficient and energy-saving separation method. These salting agents are cheap and easy to obtain, easy to recover and recycle, and the inorganic salt used will not pollute the environment. Salting-out process is featured with mild conditions and simple operation, not only saving energy consumption, but also reducing CO_2 emissions, and realizing energy saving and emission reduction.

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1 引言

生物丁醇是通过微生物的发酵而得到的产物，在本质上是自然界的整体代谢循环中的一份子[1]。丁醇作为现代化工中扮演重要角色的化工原材料，又是一种良好的有机溶剂，比如可作为油墨的溶剂；同时也能有效地增加汽油重要指标-辛烷值和含氧量的一种简单添加剂。丁醇作为待开发的、在未来可能占到主要地位的燃料对比其它现有传统石油化工燃料有如下的优点[2]。首先，丁醇作为燃料油的一个明显优点是它的能量密度是乙醇的 1.3 倍，而且由于它的饱和蒸气压低，可以加入到汽油混合物中，这将扩大它在现有汽油中的用途[3]。目前已存在的车辆能使用几乎是纯丁醇的燃油。适当调整丁醇加入汽油的比例，因而无需大幅度改造汽车便能使用，这也是丁醇作为燃油的一个不可忽视的优势，它比汽油或乙醇混合物具有更好的燃料经济性。丁醇比其他生物燃料的腐蚀性更小[4, 5]，并且可以混合到现有的混合物中高达 20%。丁醇是高能生物燃料的代表，每加仑能比传统燃料多跑 10%（1 加仑=4.5 升），比乙醇多跑 1.3 倍。它还可以提高现有乙醇汽油的性能，降低乙醇对汽油蒸气压的影响，克服现有汽油分销渠道中乙醇存在的上述问题。其次，生物丁醇主要原料——淀粉、纤维素等农产品是中国粮食主要的种植方向，生物丁醇原料价格低廉，有较大的发展空间[6, 7]。而燃烧产物很简单，水和二氧化碳，而二氧化碳会直接参与自然的碳循环，然后通过固定的粮食作物，最终又回到生物丁的原料中去，形成良性循环，是环境友好型燃料。因此，使用燃料丁醇可以从源头上防止温室效应[8, 9]。第三，生物丁醇作为一种可再生的清洁能源，是石油等化石能源的首选替代品[10]。目前，生物燃料在世界交通燃料中的比重不高，仅为 2%，但随着生物丁醇燃料的发展，未来交通燃料在主要市场中的比重可能高达 20%~30%。它是一种前景广阔、值得进一步研究的生物燃料[11–13]。

中国农业生产技术已趋于成熟，大规模种植的主要为玉米、小麦、水稻，非粮秸秆正是生产生物丁醇的基础原料。生物丁醇生产的工业发酵技术已发展成为独立的发酵、蒸馏和脱水技术。从这个意义上说，生物丁醇有条件作为一个独立的能源工业的社会和技术基础。经过近一个世纪的认识和发展，世界各国政府对生物丁醇都有不同程度的认识和研究。然而，生物丁醇的生产过程是低浓度发酵，并且会形成共沸物[14]，且分离纯化过程复杂[15]。因此，通过发酵技术或纯化方法的进步可以显着提高生物丁醇的竞争力[16–18]。

2 生物丁醇的新型分离技术

2.1 吸附分离生物丁醇

生物丁醇的吸附分离研究前人已经进行了相当多的工作。利用吸附分离丁醇的原因主要有：发酵液中生物丁醇浓度低，通常只有 18～24 g/L [19]；发酵液中产物对发酵过程有抑制作用，需通过移除发酵产物才能解决这个问题[18]。杨立荣等[19]在 1997 年已经探究了几种树脂对丁醇的吸附特性，丁醇在所研究的树脂上的吸附可用 Langmuir 方程来描述。

利用树脂来吸附生物丁醇已经研究得相当深入，并逐渐过渡到工业生产中。Moon-Ho Eom 等[20]认为各种分离技术中，吸附（使用聚苯乙烯/二乙烯基苯吸附树脂）是一种有效的节能技术，让人充满了期待。他们调查了吸附和解吸特性的发酵代谢产物来帮助设计一个新的发酵过程。Langmuir 方程和理想吸附溶液理论已经被用于开发一种吸附等温线模型，基于这一动力模型的吸附过程是完善的。通过参数估计的吸附模型，进行了一批处理混合物含有丙酮、乙醇、丁醇、乙酸、丁酸的吸附工艺实验。实验中使用的模型可以准确的预测了实际发酵液。以确保实用性，进行解吸实验。结果发现，用 140 ℃蒸汽可以使大约 95%的发酵产物得到回收。通过本研究，在吸附和解吸特性基础上，可以设计一个大型发酵罐生产并吸附提取生物丁醇。

用树脂可以有效地提取生物丁醇，但是大规模应用却有一定的难度。树脂吸附有以下优点：大孔树脂可再生、快速吸附、高吸附能力、成本低、解吸容易、潜力大、能耗低。树脂吸附的缺点有：吸附量低、不能同时回收其他成分、工序复杂，工业应用起来比较困难。

2.2 气提法分离生物丁醇

因为丙酮、乙醇和丁醇都易挥发，所以利用气提法来分离它们也是一个不错的选择。有人研究了利用氮气分离生物丁醇的效果，发现通气速率越大，冷凝收集液越多，收集液的体积与发酵液浓度无关，仅仅与通气速率有关；气提后冷凝，丁醇回收量很少，为此单单用气提不能很好地分离丁醇，需增加吸附法。冷凝液经酸处理后的竹炭吸附，100g 竹炭可吸附 0.99167g 丁醇，吸附效果良好。间歇式气提吸附可有效移除丁醇，达到分离丁醇的目的[21]。

气提法优点：可充分利用发酵过程产生的二氧化碳和氢气等气体，有效移除发酵过程中对发酵有抑制作用的产物，对发酵有利。气提法缺点：需增加氮气等气源，且后续移出溶剂丁醇、丙酮等不能有效分离，还需吸附、蒸馏等过程，仅仅对发酵有利，分离效果不佳。

2.3 薄膜渗透汽化分离生物丁醇

膜渗透蒸发降低膜后组分的蒸汽分压，提高分离液的温度，可以增加渗透过程的驱动力和组分的渗透通量，更有利于混合物的分离。

能应用于渗透汽化的膜材料有多种，无机膜和有机膜均可以，其中有机膜有聚乙烯醇（PVP）、聚四氟乙烯膜、聚丙烯膜、聚醚共聚酰胺、聚二甲硅氧烷等复合的有机硅膜等，无机膜有硅铝酸盐晶体等。他们的共同点都是让高挥发度的丁醇、丙酮、乙醇在真空的条件下通过膜组件后气化，便于回收，并且利用膜的选择性，有选择地分离产物。

聚四氟乙烯膜、聚丙烯膜可透过大量的水，液膜具有低通量和低选择性，但硅酸盐无机膜 silicalite 对发酵液具有高通量和浓缩作用。对 PDMS 膜，厚度比较薄时具有高通量和低选择性，但是比较厚时，具有高选择性和低通量。

罗建泉等[22]结果表明，丁醇发酵产物中有机溶剂的质量浓度很低。为了高效浓缩分离丁醇发酵液，采用渗透蒸发膜分离技术对模型发酵液（ABE）进行浓缩。丁醇通量随进料液温度、真空度、横流速度和质量浓度的升高而增大。当渗透蒸发膜的最佳温度为 50 ℃ 时，丁醇的选择性随真空度的降低而降低，随液体质量浓度的增加而降低。实验表明，渗透汽化法可以实现高效的丁醇分离和浓缩，并且通过串联阻力溶解扩散模型可以很好地预测 ABE 溶液体系中各组分的传质和分离效果。

渗透蒸发的优点：操作简单，环保节能，可替代传统的蒸馏、萃取、吸附等分离方法，在去除有机物或多组分混合有机物中的少量或微量水分方面具有明显的优势，可广泛应用于制药、精细化工、电子等行业的溶剂回收等诸多领域。在分离过程中，渗透蒸发不需要像蒸馏法那样将全部物料蒸发掉，而只需要将待分离的组分（如水）蒸发掉，因此渗透蒸发更加节能环保。渗透汽化法缺点：现有技术对发酵液产物分离不彻底，而且膜材料不够好，选择性不高，而且膜材料比较昂贵。

2.4 薄膜萃取分离生物丁醇

薄膜萃取分离的原理与有机溶剂萃取分离相同，均采用类似的配伍原理，但萃取剂与被萃取物之间隔有一层有机膜。

溶剂萃取过程主要取决于溶剂的极性。利用相似相容原理，通过半透膜在非极性硅树脂橡胶膜的另一侧加入乙二醇、丁醇、乙醇等水溶性萃取剂，再将丁醇、乙醇等萃取出来，达到萃取分离的目的。薄膜溶剂萃取法最大的缺点是萃取剂渗透到水相中[23]。

薄膜溶剂萃取的优点：它比简单的液液萃取要好，因为它增加了一层水不能通过的非极性膜，使水不能到达膜的另一边，萃取目的强，简单易操作。薄膜溶剂萃取的优点：平衡过程不易掌握，膜相对昂贵，溶剂会反渗透。

3 生物丁醇的盐析分离技术

3.1 盐析技术概况

传统的双水相体系由两种聚合物和水，或一种聚合物、一种无机盐和水组成[24]，广泛用于细胞、膜、酶、病毒、蛋白质、核酸等生物分子的分离[25]。最近，由于利用可再生资源生产生物基化学品和生物燃料的蓬勃发展，由有机小分子、水和盐/糖组成的新型水性两相系统正在兴起[26–29]。例如，当甲醇、乙醇[30]或其他亲水性有机溶剂[30–33]与水和无机盐以适当浓度混合时，会发生液-液相分离，从而形成新型的水两相体系。与传统萃取等分离技术相比，新型水两相体系具有操作条件温和、处理量大、易于任意规模连续操作等优点。

一般认为，无机盐的盐析作用引起了液-液相分裂[32, 34–36]。由于食盐无法在水和强极性溶剂（即甲醇或乙醇）之间产生相分离[37, 38]，因此必须转向高效的两相体系以避免溶剂损失[39]。由醇和盐组成的盐析

萃取系统通常用于从水溶液中分离增值化学品或燃料[40–45]。低溶解度盐或高溶解度盐添加不足会导致溶剂损失、产物回收不完全或盐混入有机相中[46]。因此，应根据盐析效应选择合适的盐析萃取体系。

根据 Hofmeister 系列，$CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > F^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^-$，$CO_3^{2-}$表现出最强的盐析作用。采用$(NH_4)_2SO_4$，NaCl，$NH_4Cl$，$Na_2SO_4$，$Na_3PO_4$ Na_2CO_3和$NaNO_3$等不同盐析剂对乙醇+水体系进行相分离，结果发现$(NH_4)_2SO_4$是最合适的电解质，因为它具有更强的盐析作用和更高的水溶性[47]。然而，当 40wt%的$(NH_4)_2SO_4$溶解在乙醇+水体系中时，水相含有 5wt%的乙醇[38]。在（10、30 和 50）℃下研究了乙醇+Cs_2SO_4+水系统。然而，当 Cs_2SO_4含量升至 60wt%时，水相中乙醇的质量分数约为 2wt% [48]。乙醇+$MgSO_4$/ZnSO4+水体系的液-液平衡数据在（303.15 和 313.15）K 处测定。但是表明乙醇损失的水相的乙醇含量下降得不太顺利[49]。因此，选择合适的电解质用于生物丁醇体系的相分离和较高的产物回收率至关重要。

3.2 盐析技术分离生物丁醇

在化学工业中，生物丁醇四组分混溶，精馏时又形成恒沸物，分离须经精馏，能耗大。但是经过盐析萃取后，除去大部分的水，则能降低能耗。前人已经在盐析萃取生物丁醇上面花了很多功夫。

韩晓丽[50]发现采用氟化钾对正丁醇传统生产方法进行改进，节能计算表明，新方法比传统方法节能２０％。乙醇–丙酮–丁醇–水体系的分离可使用氟化钾，但氟化钾有毒且价贵[51]。许文友[52, 53]也研究了氟化钾、碳酸钾对正丁醇发酵体系中粗醇的分离效果，但是效果还不是最佳。

前人研究了浓缩液中各种盐对生物丁醇分离的影响[54]，发现通过盐析去除水，可以显着降低工业传统精馏分离生物丁醇的高能耗。NaAc、$MgCl_2$、Na_2CO_3等盐类显着改变了正丁醇、丙酮和水体系在室温下的互溶度。研究了盐析参数对分离效率的影响，盐析与蒸馏相结合表明这种混合方法比传统方法更节能[55, 56]。盐浓度的增加有利于正丁醇与有机相的分离[43]。发现 $NaNO_2$对正丁醇具有最佳的分离效率，并将正丁醇分数从 20.8%提高到 65.24%。 各种盐对正丁醇的纯化顺序依次为：$NaNO_2$ > NaAc > K_2CO_3 > $NaNO_3$ > NaCl > $MgCl_2$ > KCl > $CaCl_2$ > Na_2CO_3 > $K_2C_2O_4$。丙酮的纯化顺序为：K_2CO_3 > Na_2CO_3 > NaAc > NaCl > $NaNO_2$ > KCl > $NaNO_3$ > $K_2C_2O_4$ > $CaCl_2$ > $MgCl_2$。各种盐对乙醇的纯化顺序依次为：K_2CO_3 > Na_2CO_3 > $NaNO_2$ > NaCl > NaAc > $CaCl_2$ > $NaNO_3$ > KCl > $K_2C_2O_4$ > $MgCl_2$。各种盐的脱水顺序依次为：K_2CO_3 > NaAc > $NaNO_2$ > NaCl > Na_2CO_3 > $NaNO_3$ > KCl > $CaCl_2$ > $MgCl_2$ > $K_2C_2O_4$。然而，水中溶解度低的盐或高溶解度盐添加不足会导致 ABE 损失、水去除低或盐混入有机相中[57-59]。

从 AEB 发酵液中盐析提取 1-丁醇的工艺节能、成本低、绿色环保。溶剂、离子和非电解质的分子间相互作用是盐析的机制[60]，它们被认为会引起水合和氢键断裂。盐析是由于温度升高而失去熵的过程。温度的升高和盐浓度的增强有利于提高盐析效果[55, 61]。

25 种化合物，包括中性盐 LiCl、$CaCl_2$、KCl、$MgCl_2$、NaCl、$NaNO_3$、K_2SO_4，酸性盐 EDTA-2Na、$AlCl_3$、$(NH_4)_2SO_4$、NH_4Cl、NaH_2PO_4、$FeSO_4$、$NaHSO_4$、$Al_2(SO_4)_3$、$MnSO_4$和碱式盐$K_2C_2O_4$、NaAc、KAc、$NaNO_2$、K_2CO_3、Na_2CO_3、Na_3PO_4、HCOONa、Na_2SiO_3已被研究作为可能的盐析剂，以从预分馏器中回收（10% 丙酮+26%丁醇+4%乙醇）[55]。只有 K_2CO_3因其无机性质、最强的盐析作用以及在水中的高溶解度而被证明是优秀的盐析剂。磷酸氢二钾（K_2HPO_4）[61]和磷酸三钾（K_3PO_4）[63]是很好的盐析剂。经过 K_3PO_4处理后，有机相的含水量从 60.00%降低到 7.11%，有机相中 1-丁醇的质量分数从 26.00%增加到 60.37%。选择焦磷酸钾（$K_4P_2O_7$）作为盐析剂时[5]当 $K_4P_2O_7$初始浓度超过 350 g/kg 时，有机相中 $K_4P_2O_7$残留量小于 300 ppm，有机相的含水量降至 5.21%，水相中丁醇的质量分数可以忽略不计。在所有研究的盐类中，$K_4P_2O_7$ 表现最好的 ABE 分离的盐析性能。K+周围的水分子形成“水合壳”，具有高极性指数，高浓度钾盐表现出显着的盐析效应，丁醇则表现出盐析作用[62]。

ABE 发酵液经醪塔浓缩后，在该塔顶部得到浓缩的 ABE 发酵液，而该塔的能耗约占整个生产车间能耗的 1/3。因此我们开发了直接从稀水溶液或发酵液中盐析 ABE 的方法[64–65]。模拟 ABE 发酵液和真实 ABE 发酵液的盐析仅实现 1-丁醇 100%回收，而乙醇和丙酮损失明显。随着盐浓度的增加，盐析效应变得更强，表明有机相中水的质量分数降低。有机相中的水含量小于 10wt%，这意味着稀 ABE 发酵液中的大部分水被去除。无论选择哪种盐析剂，均优先回收正丁醇。单组分回收率顺序为：回收率（丁醇） > 回收率（丙酮） > 回收率（乙醇）。发酵液中 ABE 浓度越高，越有利于提高

ABE 回收率，表明提高溶剂滴度对于下游工艺至关重要。

根据盐析过程后 ABE 的回收率和有机物的损失[61]，K_2HPO_4 溶液的盐析性能优于 K_2CO_3 溶液。采用盐析-精馏一体化工艺从稀发酵液中纯化 ABE [55, 56]，集成过程总能量需求的最佳值为 21.87 MJ kg^{-1} 丁醇，结果比传统工艺更节能。

4 结论

本文综述了生物丁醇的分离新技术，包括吸附、气提、薄膜渗透汽化、薄膜萃取等。对不同的分离方法进行了介绍，并对其现状及优缺点进行了评述。针对生物丁醇发酵液杂质多、目标产物多和浓度低、形成多种共沸物等分离成本和能耗高的问题，盐析法是实现目标产物分离和纯化的新型高效方法。与传统的加热或真空精馏部分发酵液相比，盐析过程改善了发酵法生产生物丁醇的传统精馏工段，节省了分离能耗。

参考文献

[1] DÜRRE P. Biobutanol: An attractive biofuel [M/OL] // Biotechnology Journal. 2007: 1525-1534. https://doi.org/10.1002/biot.200700168.

[2] KUJAWSKA A, KUJAWSKI J, BRYJAK M, et al. ABE fermentation products recovery methods - A review [M/OL] // Renewable and Sustainable Energy Reviews. 2015: 648-661. https://doi.org/10.1016/j.rser.2015.04.028.

[3] KUMAR S, CHO J H, PARK J, et al. Advances in diesel–alcohol blends and their effects on the performance and emissions of diesel engines [J/OL]. Renewable and Sustainable Energy Reviews, 2013, 22: 46-72. https://doi.org/10.1016/J.RSER.2013.01.017.

[4] XIE S, ZHANG Y, YI C, et al. Biobutanol recovery from model solutions using potassium pyrophosphate [J/OL]. Journal of Chemical Technology and Biotechnology, 2017, 92(6): 1229-1235. https://doi.org/10.1002/jctb.5113.

[5] XIE S, YI C, QIU X. Salting-out effect of potassium pyrophosphate ($K_4P_2O_7$) on the separation of biobutanol from an aqueous solution [J/OL]. Journal of Chemical Technology and Biotechnology, 2016, 91(6): 1860-1867. https://doi.org/10.1002/jctb.4779.

[6] TAO L, HE X, TAN E C D, et al. Comparative techno-economic analysis and reviews of n-butanol production from corn grain and corn stover [J/OL]. Biofuels, Bioproducts and Biorefining, 2014, 8(3): 342-361 [2022-09-05]. https://onlinelibrary.wiley.com/doi/full/10.1002/bbb.1462.

[7] TAO L, TAN E C D, MCCORMICK R, et al. Techno-economic analysis and life-cycle assessment of cellulosic isobutanol and comparison with cellulosic ethanol and n-butanol [J/OL]. Biofuels, Bioproducts and Biorefining, 2014, 8(1): 30-48. https://doi.org/10.1002/bbb.1431.

[8] MAITY S K. Opportunities, recent trends and challenges of integrated biorefinery: Part II [J/OL]. Renewable and Sustainable Energy Reviews, 2015, 43: 1446-1466. https://doi.org/10.1016/J.RSER.2014.08.075.

[9] KUITTINEN S, HIETAHARJU J, BHATTARAI I, et al. Technoeconomic analysis and environmental sustainability estimation of bioalcohol production from barley straw [J/OL]. Biocatalysis and Agricultural Biotechnology, 2022, 43(July): 102427. https://doi.org/10.1016/j.bcab.2022.102427.

[10] BANKAR S B, SURVASE S A, OJAMO H, et al. Biobutanol: The outlook of an academic and industrialist [J/OL]. RSC Advances, 2013, 3(47): 24734-24757. https://doi.org/10.1039/c3ra43011a.

[11] FU C, LI Z, SONG W, et al. A new process for separating biofuel based on the salt + 1-butanol + water system [J/OL]. Fuel, 2020, 278: 118402. https://doi.org/10.1016/j.fuel.2020.118402.

[12] TAN J, SUN Z, HUANG H, et al. Salting-out: A novel purification technique in biorefinery [J/OL]. Desalination, 2023, 564: 116790. https://doi.org/10.1016/J.DESAL.2023.116790.

[13] SUN Z, TAN J, ZHOU G, et al. Sugaring-out plus salting-out: A novel separation and purification technique for biofuel [J/OL]. Fuel, 2024, 357: 129787 [2023-09-17]. https://linkinghub.elsevier.com/retrieve/pii/S0016236123024018.

[14] STOCKHARDT J S, HULL C M. Vapor-Liquid Equilibria and Boiling-Point Composition Relations for Systems n-Butanol-Water and Isobutanol-Water [J/OL]. Industrial and Engineering Chemistry, 1931, 23(12): 1438-1440. https://doi.org/10.1021/IE50264A034.

[15] HIGASHIDE W, LI Y, YANG Y, et al. Metabolic engineering of Clostridium cellulolyticum for production of isobutanol from cellulose [J/OL]. Applied and Environmental Microbiology, 2011, 77(8): 2727-2733. https://doi.org/10.1128/AEM.02454-10.

[16] FU C, LI Z, ZHANG Y, et al. Assessment of extraction options for a next-generation biofuel: Recovery of bio-isobutanol from aqueous solutions [J/OL]. Engineering in Life Sciences, 2021, 21(10): 653-665 [2021-07-09]. https://onlinelibrary.wiley.com/doi/full/10.1002/elsc.202000090.

[17] FU C, LI Z, JIA C, et al. Recent advances on bio-based isobutanol separation [J/OL]. Energy Conversion and Management: X, 2021, 10: 100059 [2020-12-10]. https://linkinghub.elsevier.com/retrieve/pii/S2590174520300313.

[18] FU C, LI Z, SUN Z, et al. A review of salting-out effect and sugaring-out effect: Driving forces for novel liquid-liquid extraction of biofuels and biochemicals [J/OL]. Frontiers of Chemical Science and Engineering, 2020, 15: 854–871. https://doi.org/10.1007/s11705-020-1980-3.

[19] YANG L, CEN P, ZHU Z. Study on acetone/butanol fermentation with in-situ solvent extraction [J]. Journal of Zhejiang University (Natural Science), 1992, 26(4): 387-398.

[20] EOM M H, KIM W, LEE J, et al. Modeling of a biobutanol adsorption process for designing an extractive fermentor [J/OL]. Industrial and Engineering Chemistry Research, 2013, 52(2): 603-611. https://doi.org/10.1021/ie301249z.

[21] 刘佳. 气提吸附法提取丙酮丁醇工艺的研究 [D]. 河北科技大学, 2011.

[22] LUO J, YI S, SU Y, et al. Separation and concentration of butanol from acetone-butanol-ethanol mixed solution by pervaporation [J]. Chemical Engineering (China), 2010, 38(2): 43-46.

[23] GROOT W J, SOEDJAK H S, DONCK P B, et al. Butanol recovery from fermentations by liquid-liquid extraction and membrane solvent extraction [J/OL]. Bioprocess Engineering, 1990, 5(5): 203-216. https://doi.org/10.1007/BF00376227.

[24] WAN P K, LAN J C W, CHEN P W, et al. Recovery of intracellular ectoine from Halomonas salina cells with poly (propylene) glycol/salt aqueous biphasic system [J/OL]. Journal of the Taiwan Institute of Chemical Engineers, 2018, 82: 28-32. https://doi.org/10.1016/j.jtice.2017.11.003.

[25] HATTI-KAUL R. Aqueous two-phase systems: A general overview [J/OL]. Applied Biochemistry and Biotechnology - Part B Molecular Biotechnology, 2001, 19(3): 269-277. http://dx.doi.org/10.1016/B978-0-08-088504-9.00124-0.

[26] DAI J Y, SUN Y Q, XIU Z L. Separation of bio-based chemicals from fermentation broths by salting-out extraction [J/OL]. Engineering in Life Sciences, 2014, 14(2): 108-117. https://doi.org/10.1002/elsc.201200210.

[27] DAI J Y, LIU C J, XIU Z L. Sugaring-out extraction of 2,3-butanediol from fermentation broths [J/OL]. Process Biochemistry, 2015, 50(11): 1951-1957. https://doi.org/10.1016/j.procbio.2015.08.004.

[28] FU H, WANG X, SUN Y, et al. Effects of salting-out and salting-out extraction on the separation of butyric acid [J/OL]. Separation and Purification Technology, 2017, 180: 44-50. https://doi.org/10.1016/j.seppur.2017.02.042.

[29] XIE S, JIA C, WANG Z, et. al. Mechanistic Insight into Selective Deoxygenation of l -Lysine to Produce Biobased Amines [J/OL]. ACS Sustainable Chemistry & Engineering, 2020, 8(31): 11805-11817. DOI: 10.1021/acssuschemeng.0c04052.

[30] XIE S, SONG W, FU C, et al. Separation of acetone: From a water miscible system to an efficient aqueous two-phase system [J/OL]. Separation and Purification Technology, 2018, 192: 55-61. https://doi.org/10.1016/j.seppur.2017.09.056.

[31] YI C, ZHANG Y, XIE S, et al. Salting-out extraction of bio-based isobutanol from an aqueous solution [J/OL]. Journal of Chemical Technology and Biotechnology, 2018, 93(2): 372-384. https://doi.org/10.1002/jctb.5365.

[32] XIE S, ZHANG Y, ZHOU Y, et al. Salting-out of bio-based 2,3-butanediol from aqueous solutions [M/OL]//Journal of Chemical Technology and Biotechnology. 2017: 122-132. https://doi.org/10.1002/jctb.4999.

[33] XIE S, QIU X, JI W, et al. Salting-out of 1,3-propanediol from aqueous solutions by inorganic electrolytes [J/OL]. Journal of Chemical Technology & Biotechnology, 2016, 91(11): 2793-2801. https://doi.org/10.1002/JCTB.4886.

[34] SUN J, RAO B, ZHANG L, et al. Extraction of Acetoin From Fermentation Broth Using an Acetone/Phosphate Aqueous Two-Phase System [J/OL]. Chemical Engineering Communications, 2012, 199(11): 1492-1503. https://doi.org/10.1080/00986445.2012.683901.

[35] GROSS P M. The “salting out” of non-electrolytes from aqueous solutions [J/OL]. Chemical Reviews, 1933, 13(1): 91-101. https://doi.org/10.1021/cr60044a007.

[36] XIE S, LI Z, ZHU G. Salting-out Effect on the Separation and Purification of Acetic Esters: Salting-out Agents, Theory, and Applications [J/OL]. Separation and Purification Reviews, 2022 [2023-06-12]. https://www.tandfonline.com/doi/abs/10.1080/15422119.2022.2159837.

[37] MATKOVICH C E, CHRISTIAN G D. Salting-Out of Acetone from Water-Basis of a New Solvent Extraction System [J/OL]. Analytical Chemistry, 1973, 45(11): 1915-1921. https://doi.org/10.1021/ac60333a023.

[38] FU H, YANG S T, XIU Z. Phase separation in a salting-out extraction system of ethanol-ammonium sulfate [J/OL]. Separation and Purification Technology, 2015, 148: 32-37. https://doi.org/10.1016/j.seppur.2015.04.042.

[39] LYKLEMA J. Simple Hofmeister series [J/OL]. Chemical Physics Letters, 2009, 467(4-6): 217-222. https://doi.org/10.1016/j.cplett.2008.11.013.

[40] LI F, LI Q, WU S, et al. Salting-out extraction of allicin from garlic (Allium sativum L.) based on ethanol/ammonium sulfate in laboratory and pilot scale [J/OL]. Food Chemistry, 2017, 217: 91-97. https://doi.org/10.1016/J.FOODCHEM.2016.08.092.

[41] MALINOWSKI J J, DAUGULIS A J. Salt effects in extraction of ethanol, 1‐butanol and acetone from aqueous solutions [J/OL]. AIChE Journal, 1994, 40(9): 1459-1465. https://doi.org/10.1002/aic.690400905.

[42] AYDOĞAN Ö, BAYRAKTAR E, MEHMETOĞLU Ü. Aqueous two-phase extraction of lactic acid: Optimization by response surface methodology [J/OL]. Separation Science and Technology, 2011, 46(7): 1164-1171. https://doi.org/10.1080/01496395.2010.550270.

[43] WU H S, WANG Y J. Salting-out effect on recovery of 1,3-propanediol from fermentation broth [J/OL]. Industrial and Engineering Chemistry Research, 2012, 51(33): 10930-10935. https://doi.org/10.1021/ie300404t.

[44] FU C, XIE S. Salts and 1-propanol induced aqueous two-phase systems: phase separation and application [J/OL]. Journal of Chemical Technology and Biotechnology, 2019, 94(7): 2372-2381. https://doi.org/10.1002/jctb.6036.

[45] FU C, SONG W, YI C, et al. Creating efficient novel aqueous two-phase systems: Salting-out effect and high solubility of salt [J/OL]. Fluid Phase Equilibria, 2019, 490: 77-85. https://doi.org/10.1016/j.fluid.2019.03.002.

[46] RAZMARA R S, DANESHFAR A, SAHRAI R. Determination of methylene blue and sunset yellow in wastewater and food samples using salting-out assisted liquid–liquid extraction [J/OL]. Journal of Industrial and Engineering Chemistry, 2011, 17(3): 533-536. https://doi.org/10.1016/J.JIEC.2010.10.028.

[47] CAI Y, CAI Y, SHI Y, et al. A liquid-liquid extraction technique for phthalate esters with water-soluble organic solvents by adding inorganic salts [J/OL]. Microchimica Acta, 2007, 157(1-2): 73-79 [2023-11-24]. https://link.springer.com/article/10.1007/s00604-006-0625-7.

[48] HU M, ZHAI Q, LIU Z, et al. Liquid-Liquid and Solid-Liquid Equilibrium of the Ternary System Ethanol + Cesium Sulfate + Water at (10, 30, and 50)℃ [J/OL]. Journal of Chemical and Engineering Data, 2003, 48(6): 1561-1564 [2023-11-24]. https://pubs.acs.org/doi/full/10.1021/je0301803.

[49] GUO W, MA J, WANG Y, et al. Liquid-liquid equilibrium of aqueous two-phase systems composed of hydrophilic alcohols (ethanol/2-propanol/1-propanol) and MgSO 4/ZnSO 4 at (303.15 and 313.15) K and correlation [J/OL]. Thermochimica Acta, 2012, 546: 8-15. http://dx.doi.org/10.1016/j.tca.2012.07.022.

[50] 韩晓丽. 正丁醇生产新工艺 [J]. 辽宁化工, 1998(4): 44-46.

[51] CARD J, FARRELL L. Separation of alcohol-water mixtures using salts [J/OL]. 1982 [2023-11-24]. https://www.osti.gov/biblio/5250443.

[52] 许文友. 碳酸钾分离乙醇-丙酮-丁醇-水体系 [J]. 过程工程学报, 2001, 1(3): 318-320.

[53] 许文有. 用氟化钾分离乙醇－丙酮－丁醇－水体系的研究 [J]. 石油化工, 1996(01): 32-34.

[54] HU B L, QIU X Q, YANG D J. Separation of butanol-acetone-water system using repulsive extraction [J]. Huanan Ligong Daxue Xuebao/Journal of South China University of Technology (Natural Science), 2003, 31(12): 58.

[55] XIE S, YI C, QIU X. Energy-saving recovery of acetone, butanol, and ethanol from a prefractionator by the salting-out method [J/OL]. Journal of Chemical and Engineering Data, 2013, 58(11): 3297-3303. https://doi.org/10.1021/je400740z.

[56] XIE S, QIU X, YI C. Separation of a Biofuel: Recovery of Biobutanol by Salting-Out and Distillation [J/OL]. Chemical Engineering and Technology, 2015, 38(12): 2181-2188. https://doi.org/10.1002/ceat.201500140.

[57] XIE S, SONG W, YI C, et al. Salting-out extraction systems of ethanol and water induced by high-solubility inorganic electrolytes [J/OL]. Journal of Industrial and Engineering Chemistry, 2017, 56: 145-150. https://doi.org/10.1016/j.jiec.2017.07.006.

[58] HAN X. Improvement on Conventional Production of Butanol [J]. liaoning chemical industry, 1998, 04: 44-46.

[59] CEN P, TSAO G T. Recent advances in the simultaneous bioreaction and product separation processes [J/OL]. Separations Technology, 1993, 3(2): 58-75. https://doi.org/10.1016/0956-9618(93)80006-D.

[60] GROVER P K, RYALL R L. Critical appraisal of salting-out and its implications for chemical and biological sciences [J/OL]. Chemical Reviews, 2005, 105(1): 1-10. https://doi.org/10.1021/cr030454p.

[61] YI C, XIE S, QIU X. Salting-out effect of dipotassium hydrogen phosphate on the recovery of acetone, butanol, and ethanol from a prefractionator [J/OL]. Journal of Chemical and Engineering Data, 2014, 59(5): 1507-1514. https://doi.org/10.1021/je401060m.

[62] BUCHER D, KUYUCAK S. Polarization of water in the first hydration shell of K^+ and Ca^{2+} ions [J/OL]. Journal of Physical Chemistry B, 2008, 112(35): 10786-10790. https://doi.org/10.1021/jp804694u.

[63] XIE S, QIU X, YI C. Salting-out effect of tripotassium phosphate on the liquid-liquid equilibria of the (water+acetone+1-butanol+ethanol) system and the salting-out recovery [J/OL]. Fluid Phase Equilibria, 2015, 386: 7-12. https://doi.org/10.1016/j.fluid.2014.11.013.

[64] XIE S, YI C, QIU X. Salting-out of acetone, 1-butanol, and ethanol from dilute aqueous solutions [J/OL]. AIChE Journal, 2015, 61(10): 3470-3478. https://doi.org/10.1002/aic.14872.

[65] XIE S, JI W, ZHANG Y, et al. Biobutanol recovery from model solutions/fermentation broth using tripotassium phosphate [J/OL]. Biochemical Engineering Journal, 2016, 115: 85-92. https://doi.org/10.1016/j.bej.2016.08.010.