我们既要绿水青山，也要金山银山；
宁要绿水青山，不要金山银山；
而且绿水青山就是金山银山。　　——习近平主席

环保法的执行不是棉花棒，而是杀手锏。　　——李克强总理

目 录

第一章 制革废液循环利用技术介绍

制革废液循环利用技术与传统的清洁生产技术不同，该技术不需要对制革废液进行复杂的处理，可直接进行反复循环利用，目前主要应用于产污严重的浸水、浸灰和铬鞣等工序。该项技术主要优点如下：

（1）适用于大中小制革企业、各种原皮、不同风格的产品；

（2）产品质量可靠，甚至更优；

（3）大量节约用水和化料；

（4）环保效益显著，减少废水、废固物排放；

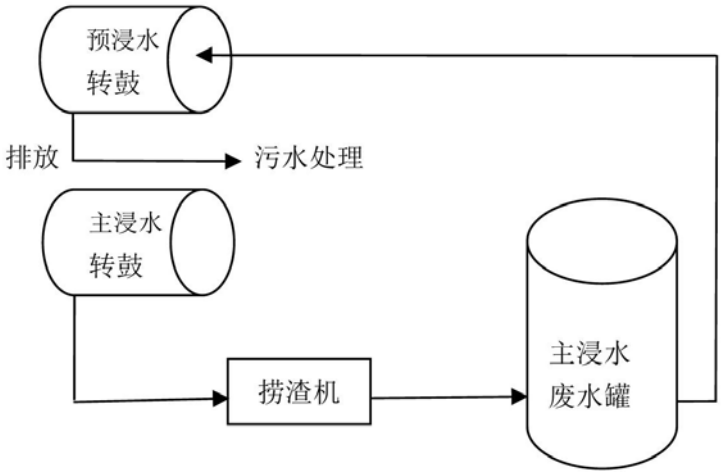
（5）改造成本低，工艺操作简便。

（6）从源头上解决制革厂因清理污水处理厂发生的伤亡事件。

一、各工序废液循环工艺介绍

1、浸水工序

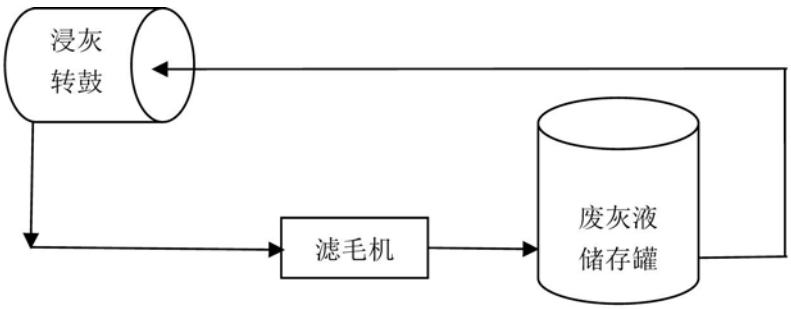
浸水工序的废液循环利用是将主浸水工序的废液收集到废液储罐，直接再次用于预浸水工序，使用时加入少量专用处理剂即可，如右图示。（注：由于浸水工序废水太脏，只循环利用一次，其它工序可反复循环利用。）



浸水工序废液循环工艺示意图

2、浸灰工序

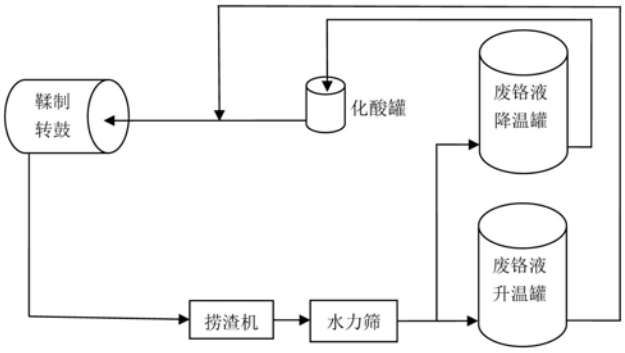
浸灰工序的废液循环利用是在灰皮出鼓前将废灰液收集到废液储罐，直接再次用于浸灰，使用时加入少量专用处理剂即可，其工艺流程示意图如下。



浸灰工序废液循环工艺示意图

3、铬鞣工序

铬鞣工序的废液循环利用是在蓝皮出鼓前将废铬液收集到废液储罐，收集时经过简单的过滤，经降温和升温后，加入少量专用处理剂，分别用于浸酸和铬鞣后期补水升温。铬鞣废液封闭循环过程中的操作液六价铬被完全抑制，废液中 Cr_2O_3、总有机碳、COD 和氨氮等含量指标随循环次数增加趋于平衡。



铬鞣工序废液循环工艺示意图

二、产品质量保证

使用废液循环技术生产的产品质量能够得到保证，包括灰皮、蓝皮各方面的质量技术指标。另外，废水做皮质量稳定可靠，不受皮源、地理区域、季节变化等因素的影响，特别是在季节交替的时候，能够保证产品质量稳定不变。

1、灰皮质量

废液循环工艺生产的灰皮质量与清水做皮相比，具备下列优势:

（1）灰皮增重率不低于清水做皮工艺，有些皮源甚至增重率更大，而且能够保证纤维松散适度，后期蓝皮不松面;

（2）灰皮膨胀均匀，纹路舒展，部位差较小;

（3）保毛质量好，滤毛效果好，毛根残留少;

（4）灰皮皮面清洁度好。

2、蓝皮及坯革质量

废液循环工艺生产的蓝皮及坯革质量与清水做皮相比，具备下列优势:

（1）蓝皮得革率提高 2%～5%，松面率降低 15%左右;

（2）收缩温度提高 2～10℃；撕裂强度提高 15%左右;

（3）蓝皮丰满度、柔软性、弹性都有明显提高，纹路舒展，粒面细致，背面绒头短、均匀。

（4）所得坯革均匀度高、部位差极小，体现在做 Nappa 摔软时，摔软时间短，背面绒毛更一致，不会出现粗绒（毛）长现象。

三、节省水和化料

由于废液中含有未被吸收的化料成分，所以该技术在节省水和化料成本方面具有显著成效，具体情况如下。

化料名称	节省比例
水	80%左右
食盐	60%以上
石灰	20%左右
硫化钠	20%～40%
硫氢化钠	30%左右
铬粉	15%-25%
注：使用废液循环工艺时，常规工艺所用的膨胀剂、石灰分散剂、浸酸油等助剂可不用，或用量大幅降低。	

四、环保经济效益显著

由于废液循环工艺生产过程中主浸水废液、废灰液、废铬液几乎全部收集利用，所以该技术在减少废固物排放、降低污水处理成本、减少环保设施投资等方面效益显著，具体情况如下。

污染物种类	减少排放比例
灰污泥（牛毛、石灰、硫化物等）	80%左右
铬污泥（铬渣、皮屑、铬化物等）	70%左右
污水中 COD、BOD	大幅度降低
污水中氯离子	大幅度降低
污水中酸类、盐类	大幅度降低
注：由于水场车间废灰液和废铬液的回收利用，后序水处理车间需要处理的污水总量大幅减少，污水有害物质浓度大幅降低，所以污水处理成本大幅降低，包括环保设备运行成本、污水处理药剂、人工成本等。	

五、技术改造成本低

由于废液循环制革工艺不需要对废液进行复杂的处理，只需将废液经过简单的过滤后收集到储罐中，直接再次使用即可，所以该项技术改造成本非常低，只需配备相应的废液收集罐、管道、抽水泵、过滤设备即可。

第二章 废液循环技术研发过程简介

一、研发过程简介

公司于 2005 年开始致力于制革废液循环利用技术的研发，先后投入近亿元资金，耗费了大量的人力、物力、财力，经过上千次的小试、中试、大试实验，于 2010 年 3 月取得重大突破，实现了废液直接循环利用技术。

该项技术的研发，打破传统的做皮观念，结合医学原理，联合国内外几家

知名科研机构和医药公司，研制出了专用处理剂，以分解抑制废液中不利于循环利用的有害成分，同时促进利用废液中对做皮有益的物质成分，使得制革废液可以反复循环利用。

在研发初期遇到了很多难题，如皮面皱纹大、毛面、烂面、扁薄、易发霉、化料难渗透、废液气味臭、废固物增多、废液粘稠度增大、循环次数少等，经过我们不懈的努力，不断进行工艺调整，研制新型化料，最终攻克了这些难题。

该技术研发成功之后，又联合四川大学、陕西科技大学、齐鲁工业大学、兴业集团进一步研发，特别是在理论方面进行完善。通过对浸灰工序和浸酸铬鞣工序废液循环的微观机理研究，结果表明废液中的相关技术指标在循环使用过程中趋于稳定，如 TOC 值、硫化物含量、粘度、铬离子含量、PH 值、盐浓度等。

二、所获专利及奖项荣誉介绍

该技术已获得国内授权发明专利 10 项，国外授权发明专利 4 项，获得省级和国家级技术奖项与荣誉称号多个，列举部分如下。

2018 年 3 月获得河南省人民政府首届发明专利奖;

2017 年 3 月获得段镇基皮革和制鞋科学技术奖;

2016 年 8 月被工信部和环保部共同列入《水污染防治重点行业清洁生产技术推广方案》;

2015 年 12 月被中国轻工业联合会授予技术发明奖;

2015 年 8 月被中国皮革协会纳入《制革行业节水减排技术路线图》;

2012 年 9 月被中国皮革协会授予节能减排环保创新奖;

2012 年 8 月被河南省发改委和环保厅评为节能减排和循环经济重点技术;

2010 年 9 月被河南省环保厅授予技术发明一等奖;

2010 年 5 月被河南省科技厅授予科学技术成果奖。

第三章 废液循环技术应用推广情况简介

一、国内应用推广情况简介

该项技术经过多年来反复的研究改进和推广应用，2012 年 7 月福建兴业皮革厂率先在大生产中使用我公司的废液循环利用技术，现已稳定运行 6 年多。

至今，已有多家企业应用了“制革废液循环技术”并实现产业化生产，如福建兴业皮革科技股份有限公司、福建瑞森皮革有限公司、黄骅德富皮革制品有限公司、徐州兴宁皮业有限公司、河北东明实业集团、焦作隆丰皮草企业有限公司、黑龙江大庆肇源皮革工业园区整体引用废液循环技术等制革厂家。

另外，亦有不少制革企业成功试用了“制革废液循环技术”并进行相关改造：如福建峰安、锦兴、致远、信德、富洋、德昌等制革厂，安徽宿松亿博工业园引入制革废液循环利用技术项目并改造完成。

为了更好的推广制革废液循环技术，在中国皮革协会和地方皮革协会、地方政府和地方环保局大力支持下，多次召开了废液循环技术研讨会和推介会（河北辛集、山东阳信、河南商丘、江苏睢宁等地），取得了良好的效果，与多家企业就使用该技术达成初步合作意向，为在我国皮革行业实现清洁化生产做出了积极的贡献。

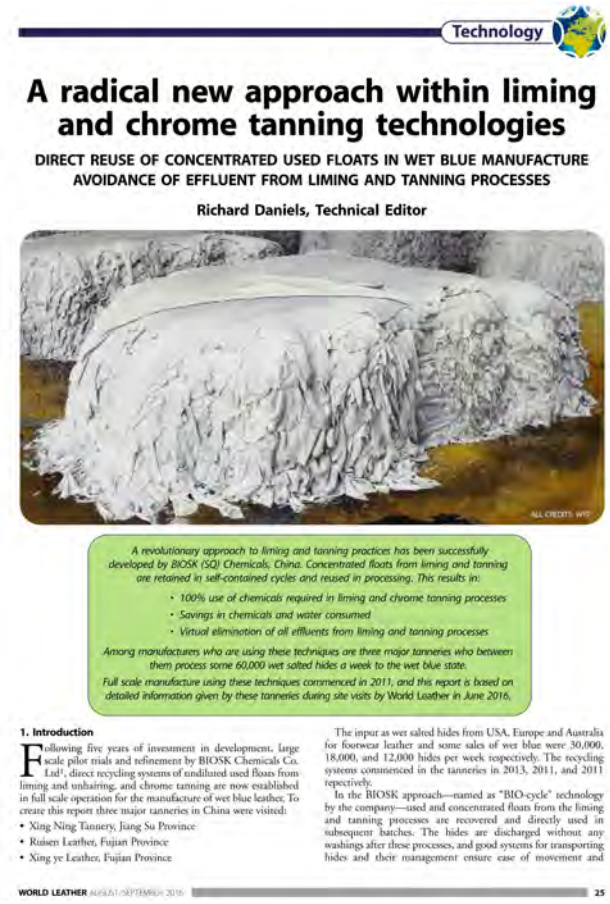
二、国外应用推广情况简介

公司技术团队于 2014 年受澳大利亚某公司邀请，前往该厂进行浸灰工序废液循环工艺大生产试验，其试验结果得到了该厂领导及工程师的充分肯定，并为我公司出具了试验结果证明。

2016 年 4 月，马其顿皮革专家 Dobre Jovanoski 前来我公司进行技术交流，对我公司的制革废液循环利用技术进行具体了解，并给予了高度赞扬。Dobre Jovanoski 在《Leather International》上发表文章，对该项技术进行了论述。

2016 年 8 月，英国皮革杂志技术主编 Richard Daniels 前来国内对制革废液循环利用技术进行调研，详细了解该项技术在大生产中的应用情况。

Richard Daniels 根据实地调研情况，在《WORLD LEATHER》上发表文章，进行了全面报道，并于 2018 年 4 月与 6 月，分别在英国皮革技师与化学家协会第 121 届国际会议上及在美国皮革化学家协会第 114 届年度会议上就该制革废液循环利用技术的作用原理以及大生产应用做了报告，引起了国际皮革行业对该技术的兴趣，提高了该项技术在国际皮革界的知名度。



Technology

A radical new approach within liming and chrome tanning technologies

DIRECT REUSE OF CONCENTRATED USED FLOATS IN WET BLUE MANUFACTURE AVOIDANCE OF EFFLUENT FROM LIMING AND TANNING PROCESSES

Richard Daniels, Technical Editor

A revolutionary approach to liming and tanning practices has been successfully developed by BIOSK (SQ) Chemicals, China. Concentrated floats from liming and tanning are retained in self-contained cycles and reused in processing. This results in:

- *100% use of chemicals required in liming and chrome tanning processes*
- *Savings in chemicals and water consumed*
- *Virtual elimination of all effluents from liming and tanning processes*

Among manufacturers who are using these techniques are three major tanneries who between them process some 60,000 wet salted hides a week to the wet blue state.

Full scale manufacture using these techniques commenced in 2011, and this report is based on detailed information given by these tanneries during site visits by World Leather in June 2016.

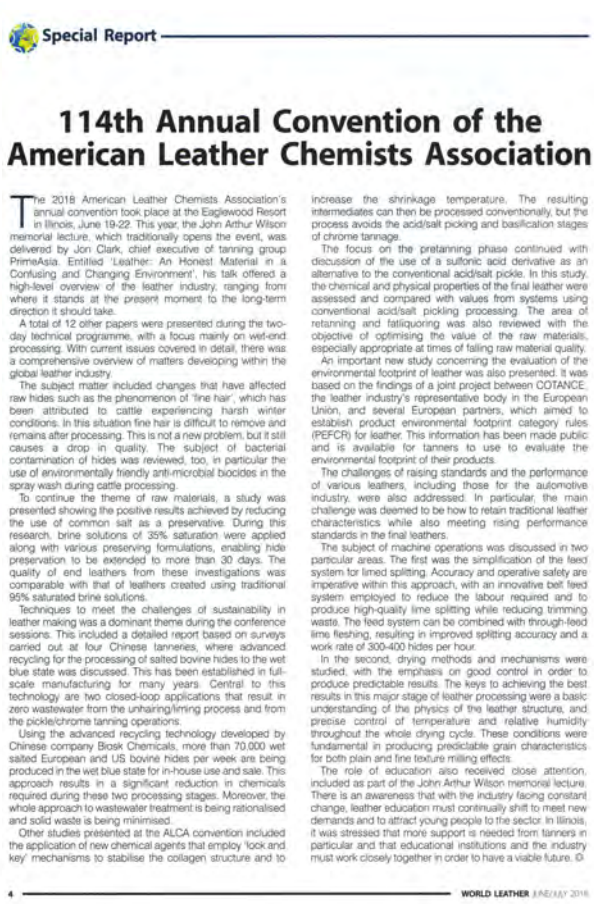
1. Introduction

Following five years of investment in development, large scale pilot trials and refinement by BIOSK Chemicals Co. Ltd[1], direct recycling systems of undiluted used floats from liming and unhairing, and chrome tanning are now established in full scale operation for the manufacture of wet blue leather. To create this report three major tanneries in China were visited:

- Xing Ning Tannery, Jiang Su Province
- Ruisen Leather, Fujian Province
- Xing ye Leather, Fujian Province

The input as wet salted hides from USA, Europe and Australia for footwear leather and some sales of wet blue were 30,000, 18,000, and 12,000 hides per week respectively. The recycling systems commenced in the tanneries in 2013, 2011, and 2011 repectively.

In the BIOSK approach—named as "BIO-cycle" technology by the company—used and concentrated floats from the liming and tanning processes are recovered and directly used in subsequent batches. The hides are discharged without any washings after these processes, and good systems for transporting hides and their management ensure ease of movement and



Special Report

114th Annual Convention of the American Leather Chemists Association

The 2018 American Leather Chemists Association's annual convention took place at the Eaglewood Resort in Illinois, June 19-22. This year, the John Arthur Wilson memorial lecture, which traditionally opens the event, was delivered by Jon Clark, chief executive of tanning group PrimeAsia. Entitled 'Leather: An Honest Material in a Confusing and Changing Environment', his talk offered a high-level overview of the leather industry, ranging from where it stands at the present moment to the long-term direction it should take.

A total of 12 other papers were presented during the two-day technical programme, with a focus mainly on wet-end processing. With current issues covered in detail, there was a comprehensive overview of matters developing within the global leather industry.

The subject matter included changes that have affected raw hides such as the phenomenon of 'fine hair', which has been attributed to cattle experiencing harsh winter conditions. In this situation fine hair is difficult to remove and remains after processing. This is not a new problem, but it still causes a drop in quality. The subject of bacterial contamination of hides was reviewed, too, in particular the use of environmentally friendly anti-microbial biocides in the spray wash during cattle processing.

To continue the theme of raw materials, a study was presented showing the positive results achieved by reducing the use of common salt as a preservative. During this research, brine solutions of 35% saturation were applied along with various preserving formulations, enabling hide preservation to be extended to more than 30 days. The quality of end leathers from these investigations was comparable with that of leathers created using traditional 95% saturated brine solutions.

Techniques to meet the challenges of sustainability in leather making was a dominant theme during the conference sessions. This included a detailed report based on surveys carried out at four Chinese tanneries, where advanced recycling for the processing of salted bovine hides to the wet blue state was discussed. This has been established in full-scale manufacturing for many years. Central to this technology are two closed-loop applications that result in zero wastewater from the unhairing/liming process and from the pickle/chrome tanning operations.

Using the advanced recycling technology developed by Chinese company Biosk Chemicals, more than 70,000 wet salted European and US bovine hides per week are being produced in the wet blue state for in-house use and sale. This approach results in a significant reduction in chemicals required during these two processing stages. Moreover, the whole approach to wastewater treatment is being rationalised and solid waste is being minimised.

Other studies presented at the ALCA convention included the application of new chemical agents that employ 'lock and key' mechanisms to stabilise the collagen structure and to increase the shrinkage temperature. The resulting intermediates can then be processed conventionally, but the process avoids the acid/salt picking and basification stages of chrome tannage.

The focus on the pretanning phase continued with discussion of the use of a sulfonic acid derivative as an alternative to the conventional acid/salt pickle. In this study, the chemical and physical properties of the final leather were assessed and compared with values from systems using conventional acid/salt pickling processing. The area of retanning and fatliquoring was also reviewed with the objective of optimising the value of the raw materials, especially appropriate at times of falling raw material quality.

An important new study concerning the evaluation of the environmental footprint of leather was also presented. It was based on the findings of a joint project between COTANCE, the leather industry's representative body in the European Union, and several European partners, which aimed to establish product environmental footprint category rules (PEFCR) for leather. This information has been made public and is available for tanners to use to evaluate the environmental footprint of their products.

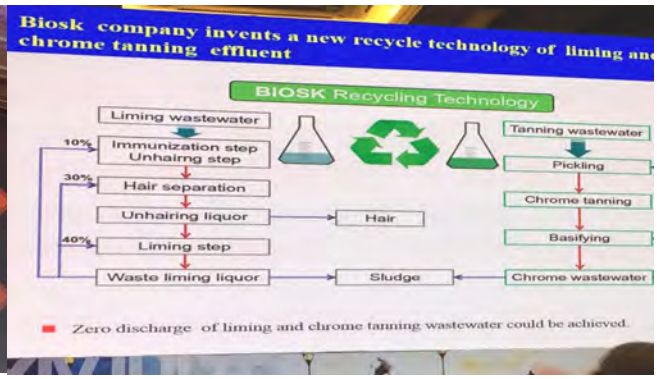
The challenges of raising standards and the performance of various leathers, including those for the automotive industry, were also addressed. In particular, the main challenge was deemed to be how to retain traditional leather characteristics while also meeting rising performance standards in the final leathers.

The subject of machine operations was discussed in two particular areas. The first was the simplification of the feed system for limed splitting. Accuracy and operative safety are imperative within this approach, with an innovative belt feed system employed to reduce the labour required and to produce high-quality lime splitting while reducing trimming waste. The feed system can be combined with through-feed lime fleshing, resulting in improved splitting accuracy and a work rate of 300-400 hides per hour.

In the second, drying methods and mechanisms were studied, with the emphasis on good control in order to produce predictable results. The keys to achieving the best results in this major stage of leather processing were a basic understanding of the physics of the leather structure, and precise control of temperature and relative humidity throughout the whole drying cycle. These conditions were fundamental in producing predictable grain characteristics for both plain and fine texture milling effects.

The role of education also received close attention, included as part of the John Arthur Wilson memorial lecture. There is an awareness that with the industry facing constant change, leather education must continually shift to meet new demands and to attract young people to the sector. In Illinois, it was stressed that more support is needed from tanners in particular and that educational institutions and the industry must work closely together in order to have a viable future.

2017 年在印度召开的第 34 届国际皮革工艺师和化学家协会联合会（IULTCS）上，中外两位专家就该制革废液循环利用技术发表专题报告，受到了与会专家的重视和好评。



第四章 制革化料与设备简介

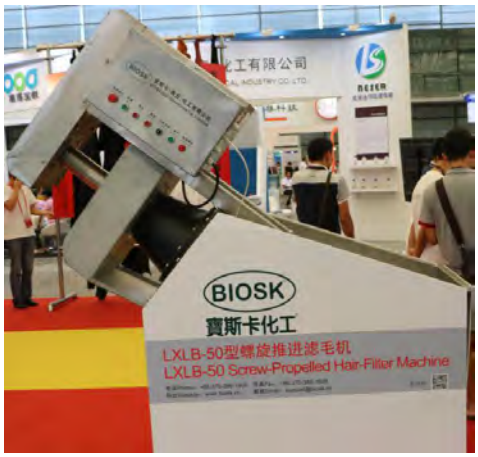
为了更好的推广制革废液循环利用技术，我公司在对该项技术进行完善升级的同时，也在不断投入大量资金进行制革化料及废液循环配套设备的研发与更新。

一、化料简介

在化料研发方面，结合医学原理，独辟蹊径，开发了性能独特的产品，有浸水剂、浸灰剂、杀菌剂、防霉剂、脱灰剂、脱脂剂、提碱剂、酶制剂、鞣制助剂、复鞣染色助剂、废液循环专用处理剂等化料产品系列，处于国际领先水平，在业内知名度非常高，畅销国内外。

二、滤毛机、智能固液分离机等环保设备简介

现在浸灰工序大多采用保毛滤毛工艺，以减少污水中的有机物含量，有利于污水处理。特别是使用废液循环利用技术，配合我公司生产的滤毛机、多效微粒筛等环保设备，能够大大降低废水中的 COD、BOD 指标。



螺旋推进式滤毛机，具有滤毛速度快、牛毛含水少、运行平稳、耐用、性价比高等特点。

设备整体采用 316L 不锈钢材质；螺旋叶片加工精密；轴下部的滑动轴承采用进口耐磨材料，经久耐用，运行平稳；橡胶锥套采用高弹性耐酸碱橡胶材质；选用全不锈钢排污泵，流量大，不易堵塞；采用电气自动控制，安全可靠。

智能固液分离机能有效地去除液体中的悬浮物、漂浮物、沉淀物等固态物质，降低固体颗粒的浓度，将固液分离，适用于制革、毛皮、化工、制药、食品饮料等行业。

具有智能化、防堵塞、耐酸碱腐蚀、过滤精度高、滤渣干等优点。