water

MDPI

Technical Note

Water Footprint and Water Pinch Analysis in Ethanol Industrial Production for Water Management

Heng Liu, Lijun Ren *, Huimin Zhuo and Sanze Fu

School of Environmental Science and Engineering, Shandong University, Qingdao 250100, China; 201612038@mail.sdu.edu.cn (H.L.); 201732605@mail.sdu.edu.cn (H.Z.); 201712529@mail.sdu.edu.cn (S.F.)

* Correspondence: ljren@sdu.edu.cn; Tel.: +86-135-7310-7765

Received: 29 January 2019; Accepted: 9 March 2019; Published: 12 March 2019

check for updates

Abstract: Fuel ethanol is considered to be a clean alternative fuel to meet increasing energy demands and mitigate environmental pollution. Faced with challenges in terms of energy security and environmental pollution, China is vigorously developing fuel ethanol. However, ethanol-manufacturing is a water-intensive industry; it consumes large volumes of fresh water and generates a corresponding amount of waste water. Expansion of this industry can reduce water quality and cause water stress. This study aims to combine the water footprint (WF) with a water pinch analysis technique to manage water consumption and sewage discharge systematically in an ethanol plant. A well-operated cassava ethanol plant in China was chosen as a case study. The WF of industrial ethanol production was evaluated. The total WF was 17.08 L/L ethanol, comprised of a 7.69 L blue water footprint (BWF), and a 9.39 L gray water footprint (GWF). The direct WF was 16.38 L/L ethanol, and the indirect WF was 0.70 L/L ethanol. Thereafter, a water pinch analysis was conducted, and the optimal direct water reuse scheme was studied. After the water network was optimized, the BWF was reduced by 0.98 L/L ethanol, while the GWF was reduced by 1.47 L/L ethanol. These results indicate that the combined use of WF and pinch analysis can provide the starch-based ethanol industry with an effective tool to improve its water management.

Keywords: ethanol production; water footprint; water pinch analysis; water management

1. Introduction

Fuel ethanol is a kind of renewable energy. Fuel ethanol can be blended with gasoline to form ethanol gasoline. Ethanol contains 35% oxygen, which enables a more efficient burning of gasoline, resulting in reduced emissions of particulate matter (PM), nitrogen oxides, hydrocarbons, and carbon monoxide [1]. Bioethanol has been widely used in several countries, including the United States, Brazil, Thailand, China, Australia, and Mexico. In China, fuel ethanol production was initiated late but is developing rapidly. Currently, China has become the third largest producer of fuel ethanol after Brazil and the United States.

China is rapidly developing its fuel ethanol industry for the following two reasons: (1) to ease the energy constraint on the economy. China relies heavily on imported oil to meet its energy demands and high prices of the imported oil are threatening China's energy security [2]; (2) to alleviate air pollution. Fossil fuel combustion is widely considered as one of the primary causes of air pollution. Vehicles are a major contributor to air pollution emissions in China [3]. In 2017, the Chinese government proposed promoting the use of ethanol gasoline, and the complete replacement of conventional gasoline in 2020.

However, the use of fuel ethanol is also beset by two controversial issues: whether it is environmentally friendly and whether it produces positive net energy [4]. In previous studies, many ethanol production systems have been assessed with a life cycle assessment across various categories, including its energy balance, greenhouse gas emissions, environmental pollution and water footprint [5–9]. The conclusion of these studies was that the use of bioethanol leads to a net gain and greenhouse gas emissions decrease. Divergent conclusions were reached concerning whether it is environmentally friendly because of different approaches, scope, farming practices, and ethanol conversion technologies [7]. Biofuel production can benefit rural economies [10] and the importance of the biofuel sector and the complexity of the systems are expected to increase [11].

Water and energy systems are closely related. Generally, the production of energy consumes high quantities of water. The term "water-energy nexus" is highly relevant to sustainable water management [12]. As the production of bioethanol is gaining impetus, water consumption and pollution are correspondingly increasing. Ethanol-manufacturing is an intensive water-consuming industry. Previous studies have demonstrated that fresh water consumption for producing 1 ton of ethanol ranged between 15–30 tons [13]. The effluent discharged by ethanol plant may range from 12−15 L/L ethanol (liter per liter ethanol) [14], or 6−20 L/L ethanol [15]. The effluent contains a large amount of biological oxygen demand (BOD), chemical oxygen demand (COD), and total dissolved solids (TDS) [16]. Water consumption and effluent discharge during ethanol production can cause water quality to deteriorate, leading to water stress [17]. Amid tighter environmental regulations for discharged waste water, more effort is being devoted to reducing water consumption. However, water management in ethanol plants is usually based on intuition, combined with empirical observation. Therefore, systematic reductions of fresh water consumption and effluent discharge are problematic. An effective water management strategy is required to conserve water resources. In this study, water footprint (WF) and water pinch analyses were combined to provide ethanol manufacturing industries with a water management tool that can reduce both fresh water consumption and effluent discharge.

Hoekstra and Chapagain proposed and developed the concept of a WF [18]. They defined the WF of a product as the total volume of fresh water consumed across the entire value chain of production. Previous studies of WF have investigated the water footprints of ethanol production [19–23] but most of them focused on calculating the WFs of feedstocks; few have reported the WF at an industrial scale. In this study, the WF of ethanol production on an industrial scale was calculated and used as an evaluation indicator for water integration. The water footprint analysis focused on the industrial production of ethanol in the production plant; the water footprint of the biofuel feedstock production was not included.

A water pinch analysis is a methodology of water integration for minimizing water consumption in industrial production processes by calculating the minimum fresh water consumption and realizing it via optimization of water systems. In 1994, Wang and Smith proposed the concept of water pinch, along with many other important concepts, including a limiting composite curve and a water supply line [24,25]. The water pinch methodology has been successfully applied to optimize the water systems in various industries, including the chemical industry [26], oil refineries [27,28], the steel industry [29], and others. Particularly in the steel industry, China has issued the *Water System Integration and Optimization of Steel Industry Implementation Guide*, which established the central importance of water pinch analysis in the steel industry for water system integration, and accelerated the application of water pinch analysis in steel enterprises. However, few studies of the application of water pinch analysis in the ethanol industry have been reported thus far. This study aimed to explore the application of the water pinch analysis to an ethanol production plant in order to optimize the water network and investigate the potential of this technique to systematically reduce the water footprint.

The remainder of this paper is structured as follows. The methodology for conducting water footprint assessment and the water pinch analysis is described in Section 2. The case study of an ethanol production plant is described in Section 3 and the results are presented in Section 4. Thereafter, Section 5 describes the water pinch analysis as conducted, and the optimization of the water network. The results of water footprint reduction on the water pinch analysis are discussed in Section 6.

2. Materials and Methods

2.1. Industrial Water Footprint Assessment

The water footprint is divided into three parts: blue water, green water, and grey water. Blue water is the water stored in rivers, lakes, wetlands, and shallow underground aquifers. Green water is rainwater consumed by evapotranspiration through vegetation associated with the industry. Gray water is the water that is polluted across the entire value chain.

The water footprint of industrial production is also divided into a direct water footprint and an indirect water footprint. The direct water footprint is the water footprint directly used in ethanol production, and the indirect water footprint is the water footprint of auxiliary materials and energy consumed. The equations for determining WF and WF_{direct} are as follows:

$$WF = WF_{direct} + WF_{indirect} \tag{1}$$

$$WF_{direct} = BWF_{direct} + GWF_{direct} \tag{2}$$

where WF is total water footprint, WF_{direct} is the direct water footprint, and $WF_{indirect}$ is the indirect water footprint. $BWF_{dircect}$ and GWF_{direct} are the direct blue-grey water footprints, respectively.

The $BWF_{dircect}$ of alcohol production is the amount of mains water consumed directly in the production processes. It is obtained by subtracting the return water flow from the water inputs and dividing by the ethanol output per day. It can be calculated using Equation (3):

$$BWF_{direct} = \frac{F_{fresh\ water} - F_{return}}{M_{ethanol}} \tag{3}$$

where $F_{fresh\ water}$ is the flow rate of total fresh water input, F_{return} is the return water flow rate, $M_{ethanol}$ is the output of ethanol per day.

The direct grey water footprint is the volume of water required to dilute the effluent in order to meet the environmental water quality standards of the receiving water body. As water bodies that have diluted one kind of pollutant can continue to dilute another kind of pollutant, the final gray water footprint is determined by the pollutant with the largest grey water footprint. The direct grey water footprint can be calculated using Equations (4) and (5):

$$GWF_{direct} = \max\{GWF_{1-direct}, GWF_{2-direct}, \cdots, GWF_{i-direct}\} \tag{4}$$

$$GWF_{i-direct} = \frac{V_{effl}(C_{i-eff} - C_{i-nat})}{(C_{i-max} - C_{i-nat})} \tag{5}$$

where $GWF_{i-direct}$ is the direct gray water footprint of pollutant *i*. V_{effl} is the effluent volume, C_{i-eff} is the concentration of pollutant *i*. C_{i-nat} is the natural concentration of pollutant *i* in the receiving water body. The natural concentration is the concentration in a water body if it was in the original state, before human disturbances in the catchment. When natural concentrations are not known precisely but are estimated to be low, for simplicity one may assume $C_{nat} = 0$ [30]. However, the real value of the background concentration is not zero; therefore the results for the corresponding gray water footprint will be smaller than the actual value. C_{i-max} is the maximum acceptable concentration of pollutant *i*.

Auxiliary materials, including amylase, glucoamylase, and yeast, which are involved in the industrial production of ethanol, make only a limited contribution towards the product water footprint, and the calculation of their relative contribution is very difficult. In the production of 1 ton of ethanol, the consumption of amylase, glucoamylase and yeast is 1.9 kg, 3.7 kg, and 0.02 kg, respectively. We roughly estimated that the water footprint for using the enzymes and yeast were not significant compared to the water footprint of energy. Therefore, auxiliary materials were not included in the calculation.

$$WF_{indirect} = BWF_{erengy} + GWF_{erengy}. \tag{6}$$

The calculation of the water footprint energy is based on the methods of Yan et al. [31].

2.2. Optimization of The Water Network

Prior to designing the network, the limiting composite curve was used to determine the water pinch point, which is the point of minimum fresh water consumption. The mass problem table was proposed by Castro and co-workers as an alternative technique for setting the minimum fresh water targets [32]. An improved targeting approach, based on the principle of nearest neighbors, to achieve the minimum fresh water has been proposed [33]. Limiting composite curves that are usually used in the water pinch analysis can directly identify the location of a water pinch point. However, when there is a large number of water units and the concentration span is large, the use of a composite curve is too tedious and inaccurate. The concentration interval diagram (CID), which is a type of mass problem table, was used to determine the accurate location of the pinch point.

The CID used to determine the minimum fresh water amount of the system included the following steps:

1. The inlet and outlet concentrations of all units were arranged from small to large to form concentration intervals.
2. For a given concentration interval k, the pollution mass transfer load $m_{i,k}$ for each water operation in the interval was calculated and the total mass load m_k within interval k was obtained.

$$m_{i,k} = f_i(C_{k+1} - C_k) \tag{7}$$

$$m_k = \sum_i f_i(C_{k+1} - C_k). \tag{8}$$

3. The cumulative mass load at the end of each interval was calculated in ascending order of intervals, and the mass transfer load at each interval was summed.

$$\Delta m_k = \sum_k m_k \tag{9}$$

4. The flow rate at each interval boundary was calculated according to the accumulated mass load and the interval boundary concentration.

$$f_k = \frac{\Delta m_k}{C_k} \times 10^3. \tag{10}$$

In the last column of the CID, the largest water supply flow rate is the fresh water pinch point. Then, the water network was optimized via *Water Design* software.

3. Case Study

The main feedstocks for bioethanol production in China are starch-containing crops such as corn, wheat, and cassava [34]. China has banned the use of food crops in new ethanol factories because of the conflict between food security and ethanol production. Consequently, non-edible feedstocks such as cassava are encouraged. Furthermore, current lignocellulose feedstock ethanol conversion technologies are not yet able to meet the demand for ethanol in an economically viable manner [35]. Thus, a well-operated cassava ethanol production plant in Shandong Province was investigated in the present study.

This plant produces 106.06 tons of ethanol per day and consumes 1156.17 t/d of fresh water, discharges 659 t/d of waste water, and utilizes 170.73 Kwh/t of ethanol. Fresh water withdrawal is 11 t/t product, which is close to the cleaner production level 1 standard (10 t/t ethanol) of China. Sewage is discharged after it is treated to meet the “discharge standard of water pollutants for fermentation alcohol and distilled spirits industry". The water network of the plant is shown in Figure 1 and details on the flow rate of each water-using unit are shown in Table 1.

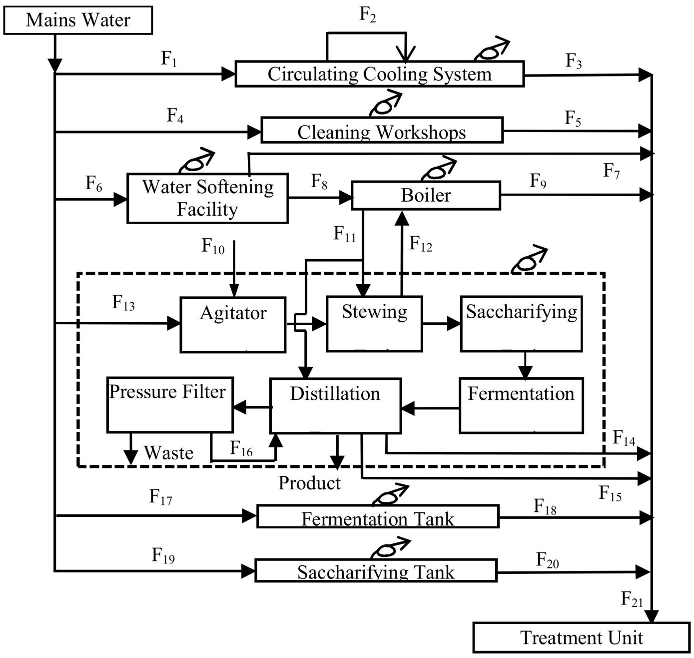

Figure 1. Flow chart of the water-using units at the bioethanol production plant. ‾‾‾: Ethanol production zone; : Water loss by evaporation and drift.

Table 1. Description and flow rate of the water-using units of the bioethanol production plant.

Number	Description	Flow Rate (t/d)
F_1	Mains water used to circulate cooling water	229.18
F_2	Recirculating cooling water	170.22
F_3	Circulating cooling water blowdown	58.19
F_4	Mains water used to clean workshops	26.22
F_5	Waste water after cleaning workshops	8.13
F_6	Mains water used to prepare soft water	85.90
F_7	Concentrated water	15.93
F_8	Boiler feed water	68.92
F_9	Boiler sewage	11.84
F_{10}	Moisture content of cassava	20.57
F_{11}	Steam for production process	130.16
F_{12}	Steam condensate returns to the boiler	72.88
F_{13}	Mains water for ethanol conversion process	809.67
F_{14}	Steam condensate	64.95
F_{15}	Ethanol stillage	419.86
F_{16}	Recycling filtrate of stillage	239.82
F_{17}	Mains water used to clean the facilities	61.83
F_{18}	Waste water from cleaning the facilities	58.13
F_{19}	Mains water to sterilize the saccharifying tank	12.94
F_{20}	Waste water after sterilization of the saccharifying tank	12.11
F_{21}	Discharged treated water	649.14

Water with high COD levels could cause equipment corrosion, according to the *Code for Design of Cooling for Industrial Recirculating Water* and a high COD load associated with effluent causes the main difficulties in treating the latter [36]. Therefore, COD was selected as the pollutant index for the gray water footprint and key contaminant for water pinch analysis, combining the requirements of both [26].

4. Water Footprint Analysis

4.1. System Boundary and Calculation Method

This analysis is based on the concept of the industrial water footprint and its evaluation framework. The system boundary for evaluating the water footprint of the industrial ethanol production stage in a factory accounts for inputs (water, steam, and energy) and outputs (effluent, waste, and product). The water used by staff and the consumption of water resources to produce goods supplied by agriculture, forestry, animal husbandry, fisheries, and natural ecosystems were not included in the evaluation [37]. The system boundary of industrial water footprint evaluation is shown in Figure 2.

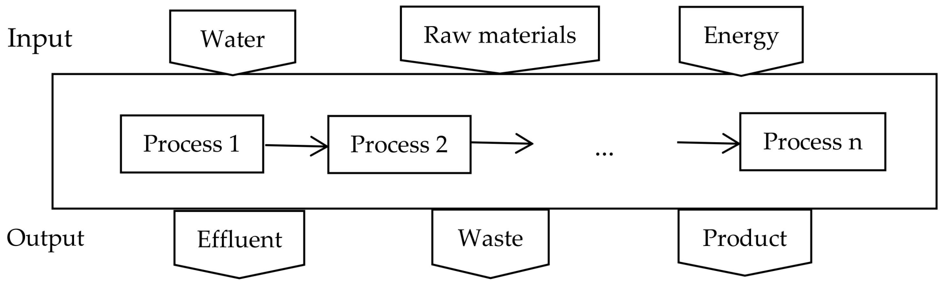

Figure 2. System boundary of ethanol industrial water footprint.

4.2. Results and Analysis of Water Footprint Calculation

In calculations of the industrial water footprint, the green water footprint mainly comes from the use of collected rainwater. This plant does not collect rainwater, so the green water footprint was ignored. As shown in Figure 3, the WF of the ethanol plant was 17.08 L/L ethanol. The BWF was 7.69 L/L ethanol, which is less than the 8.30–18.97 L/L ethanol BWF of a cassava-based ethanol plant in Thailand [38], and close to the result of a study in Guangxi, which was 7.60 L/L ethanol [13]. The GWF in the study plant was 9.39 L/L ethanol, which is less than the 11.46 L/L ethanol resulting from the study in Guangxi because the sewage and polluted process water were treated to a high standard before discharge to the receiving water body. All these points illustrate the study plant has a good level of water management.

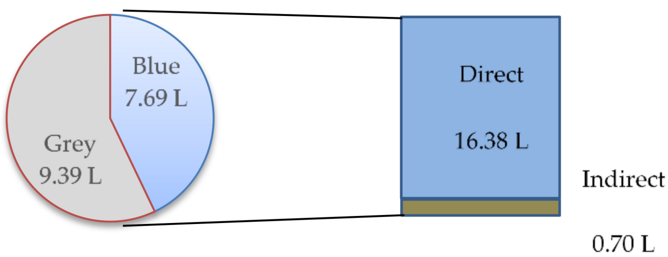

Figure 3. The water footprint of 1 L of ethanol.

As shown in Figure 4, the direct WF was 16.38 L/L ethanol; this accounted for 96% of the total water footprint. The direct BWF was 7.19 L/L ethanol, dominated by the water used in the ethanol conversion process. The direct GWF was 9.19 L/L ethanol, dominated by the WF of ethanol stillage discharge. Therefore, recycling the filtrate of stillage via fermentation could significantly reduce both the direct BWF and direct GWF. The stillage has a substantial COD and acidic and corrosive characteristics [39] and thus methods for recirculation of stillage need to be implemented in the industry. In the current case study, 40% of the filtrate of ethanol stillage was recirculated, which is a considerable fraction of the total.

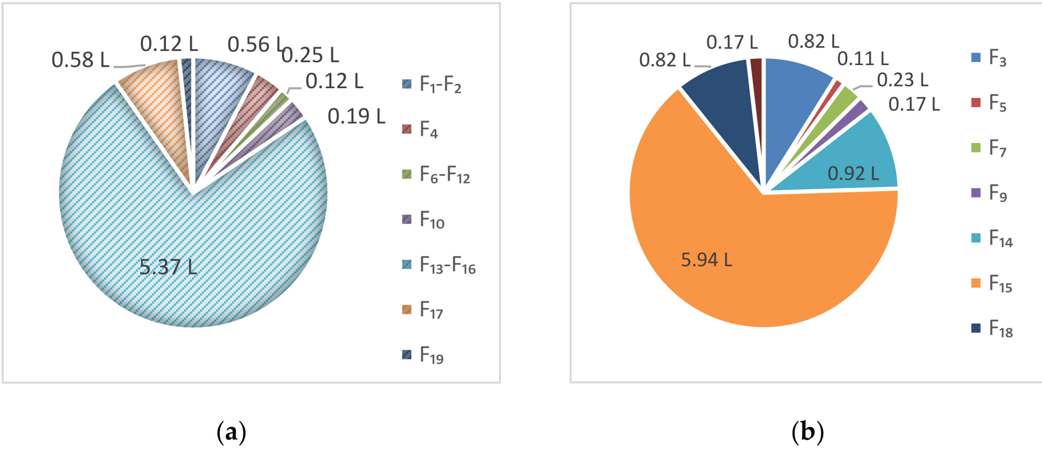

Figure 4. The direct water footprint of 1 L ethanol per production process. (**a**) Direct blue water footprint; (**b**) direct gray water footprint.

5. Water Pinch Analysis

5.1. Analysis of Operations Using Water

The circulating cooling water and steam do not come into contact with the materials used to produce ethanol. Therefore, the COD of the circulating cooling water and steam condensate was low and these can be reused directly in other units. The main purposes of the facility cleaning and sterilization processes are, respectively, washing away any residual substances and killing hybrid bacteria to ensure that the next fermentation is not affected. As the water quality requirement is not too high, reused water can be considered for these processes. Workshop cleaning also has a low water quality requirement and the final waste water is sent to the sewage treatment station for treatment; thus, relatively clean discharge sewage can be considered for direct reuse. A water pinch analysis was conducted on these five operations. The limiting concentration was obtained from the equipment manufacturer, the *Code for Design of Cooling for Industrial Recirculating Water*, and the *Miscellaneous Urban Water Quality Standard*, as shown in Table 2.

Table 2. Water using operations summary for water pinch analysis.

Operation Number	Description	Flow Rate (te/hr)	Limiting Inlet Concentration (COD; ppm)	Limiting Outlet Concentration (COD; ppm)
Operation 1	Circulating cooling	2.42	5.00	100.00
Operation 2	Workshops cleaning	1.09	60.00	1500.00
Operation 3	Steam condensate	2.70	0.00	20.00
Operation 4	Facilities cleaning	2.58	50.00	1000.00
Operation 5	Sterilization	0.50	50.00	400.00

Note: The unit "te/hr" denotes "tonne per hour".

5.2. Determining the Pinch Concentration

In Table 3, arrows are used to indicate the direction of the contaminant load transfer. The concentration of the water pinch point was 4.92 te/hr.

Table 3. Concentration interval diagram of the water system.

Concentration (ppm)	Operation 1 2.42 te/hr	Operation 2 1.09 te/hr	Operation 3 2.70 te/hr	Operation 4 2.58 te/hr	Operation 5 0.50 te/hr	Mass Load (kg/hr)	Cumulative Mass Load (kg/hr)	Flowrate (te/hr)
0							0.00	0.00
						0.01		
5.00							0.01	2.70
						0.08		
20.00							0.09	4.52
						0.07		
50.00							0.16	3.26
						0.05		
60.00							0.22	3.63
						0.26		
100.00							0.48	4.92
						1.25		
400.00							1.73	4.33
						2.20		
1000.00							3.93	3.93
						0.55		
1500.00							4.48	2.99

5.3. Optimizing the Water Network

The preliminary block diagram concentration-interval boundaries, which included the reuse water operation, was created using the software Water Design, as shown in Figure 5. The water discharged by operation 3 can be reused in all other operations, and the water discharged by operation 1 can be reused in operations 2, 4, and 5. The volume of water lost was very small and therefore, it was ignored in the diagram.

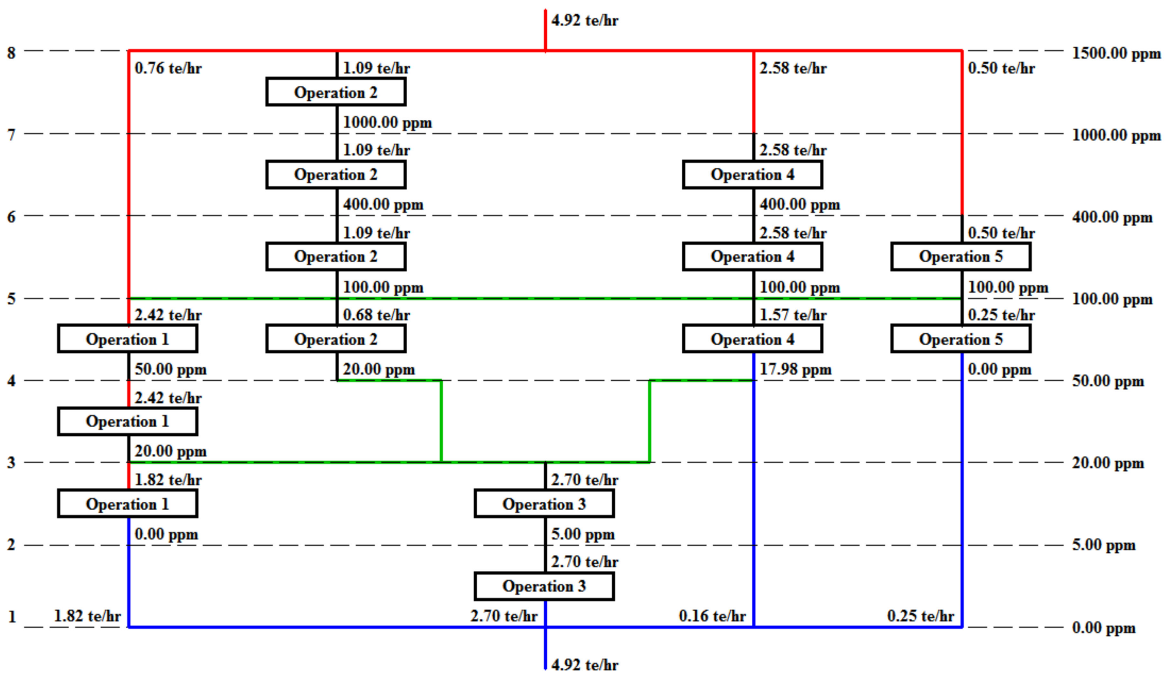

Figure 5. Preliminary block diagram concentration-interval boundaries. The blue, green, and red lines represent fresh water, water reuse, and effluent streams, respectively.

The water network was then optimized, as shown in Figure 6. The flow rate of reused water from operation 3 to operation 5 was very low and it was therefore replaced by fresh water. The final minimum fresh water consumption was 4.97 te/hr. Furthermore, because water loss was ignored, the effluent discharged was also 4.97 te/hr.

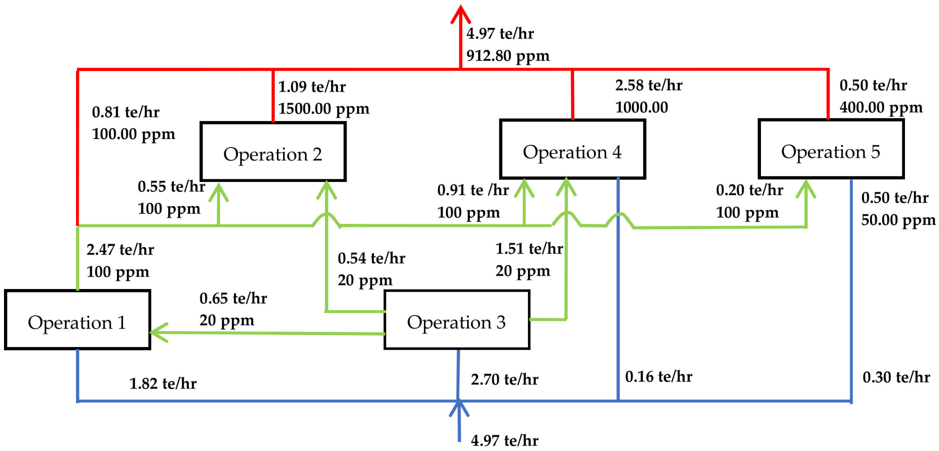

Figure 6. Evolution of the water network evolution. The blue, green, and red lines represent fresh water, water reuse, and effluent streams, respectively.

6. Water Footprint Reduction on Water Pinch Analysis

After the water network was optimized as described above, fresh water consumption was reduced by 4.32 te/hr. The WF was calculated using the methods in Section 3. The BWF was reduced by 0.98 L/L ethanol, which is 12.7% of its original value. The GWF was reduced by 1.47 L/L ethanol, which is 15.7% of its original value. Given that the case study plant manages water very well and that no additional water treatment facility was required, the results show that the water pinch analysis technique is an effective strategy to reduce the water footprint. As all starch-based ethanol manufacturing processes are similar, water footprint and water pinch analyses can be combined as a water management tool and expanded to other ethanol plants.

7. Conclusions

This study concentrated on assessing the water footprint of ethanol production and optimizing the water system by conducting water pinch analysis. The water network of processes in a well-operated cassava ethanol plant was established and an industrial water footprint assessment was conducted. The current industrial water footprint of ethanol is 17.08 L/L ethanol, consisting of a 7.69 L blue water footprint and a 9.39 L gray water footprint. The latter would be higher if no waste water treatment occurred. The water consumed in the ethanol conversion process contributed the most to the blue water footprint and ethanol stillage contributed the most to the gray water footprint. Consequently, the overall water footprint could be greatly reduced by recirculating the filtrate of ethanol stillage. A water pinch analysis was also performed to optimize the water system of the ethanol plant, resulting in a 0.98 L reduction in the blue water footprint and a 1.47 L reduction in the gray water footprint. Consequently, the industrial water footprint of ethanol was 14.63 L/L ethanol, 23.2% less than the 19.06 L/L ethanol resulting from a well-operated system in Guangxi [13]. These results demonstrated that this method can be used as an effective water management tool in cassava ethanol plants. Because the production processes of all starch-based ethanol plants are similar [40], this method can be expanded to other facilities.

The large amount of thermal energy used in ethanol plants also limits the minimum water consumption that can be achieved. Heat exchange network optimization can reduce the water footprint by decreasing the consumption of energy, steam, and cooling water. Water integration should be combined with heat integration and applied in bioethanol plants to further improve water management.

Author Contributions: Conceptualization, H.L. and L.R.; methodology, H.L.; software, H.L.; validation, H.L., L.R. and H.Z.; formal analysis, S.F.; investigation, H.L.; resources, L.R.; data curation, H.L.; writing—original draft

preparation, H.L.; writing—review and editing, H.L., H.Z. and S.F.; visualization, H.L.; supervision, L.R.; project administration, L.R.; funding acquisition, L.R.

Funding: This research was funded by the National Key Research and Development Program of China, grant number 2017YFF0206702.

Acknowledgments: The authors thank Hui Song for help in data processing.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Balat, M.; Balat, H. Recent trends in global production and utilization of bio-ethanol fuel. *Appl. Energy* **2009**, *86*, 2273–2282. [CrossRef]
2. Zhao, X.; Liu, P. Focus on bioenergy industry development and energy security in China. *Renew. Sustain. Energy Rev.* **2014**, *32*, 302–312. [CrossRef]
3. Sun, S.; Fang, C.; Lv, J. Spatial inequality of water footprint in China: A detailed decomposition of inequality from water use types and drivers. *J. Hydrol.* **2017**, *553*, 398–407. [CrossRef]
4. Leng, R.; Wang, C.; Zhang, C.; Dai, D.; Pu, G. Life cycle inventory and energy analysis of cassava-based Fuel ethanol in China. *J. Clean. Prod.* **2008**, *16*, 374–384. [CrossRef]
5. Yu, S.; Tao, J. Economic, energy and environmental evaluations of biomass-based fuel ethanol projects based on life cycle assessment and simulation. *Appl. Energy* **2009**, *86*, S178–S188. [CrossRef]
6. Liu, B.; Wang, F.; Zhang, B.; Bi, J. Energy balance and GHG emissions of cassava-based fuel ethanol using different planting modes in China. *Energy Policy* **2013**, *56*, 210–220. [CrossRef]
7. Silalertruksa, T.; Gheewala, S.H. Environmental sustainability assessment of bio-ethanol production in Thailand. *Energy* **2009**, *34*, 1933–1946. [CrossRef]
8. Papong, S.; Malakul, P. Life-cycle energy and environmental analysis of bioethanol production from cassava in Thailand. *Bioresour. Technol.* **2010**, *101* (Suppl. 1), S112–S1128. [CrossRef]
9. Kim, S.; Dale, B. Ethanol Fuels: E10 or E85–Life Cycle Perspectives (5 pp). *Int. J. Life Cycle Assess.* **2005**, *11*, 117–121. [CrossRef]
10. Ishola, M.M.; Brandberg, T.; Sanni, S.A.; Taherzadeh, M.J. Biofuels in Nigeria: A critical and strategic evaluation. *Renew. Energy* **2013**, *55*, 554–560. [CrossRef]
11. Miglietta, P.P.; Giove, S.; Toma, P. An optimization framework for supporting decision making in biodiesel feedstock imports: Water footprint vs. import costs. *Ecol. Indic.* **2018**, *85*, 1231–1238. [CrossRef]
12. Miglietta, P.; Morrone, D.; De Leo, F. The Water Footprint Assessment of Electricity Production: An Overview of the Economic-Water-Energy Nexus in Italy. *Sustainability* **2018**, *10*, 228. [CrossRef]
13. Zhang, T.; Xie, X.; Huang, Z. The policy recommendations on cassava ethanol in China: Analyzed from the perspective of life cycle "2E&W". *Resour. Conserv. Recycl.* **2017**, *126*, 12–24. [CrossRef]
14. Pant, D.; Adholeya, A. Biological approaches for treatment of distillery wastewater: A review. *Bioresour. Technol.* **2007**, *98*, 2321–2334. [CrossRef]
15. Tewari, P.K.; Batra, V.S.; Balakrishnan, M. Water management initiatives in sugarcane molasses based distilleries in India. *Resour. Conserv. Recycl.* **2007**, *52*, 351–367. [CrossRef]
16. Handelsman, T.; Kavanagh, J.; Coster, H.; Barton, G. Zero discharge fermentation plant design. *Desalin. Water Treat.* **2011**, *34*, 389–393. [CrossRef]
17. Dominguez-Faus, R.; Powers, S.E.; Burken, J.G.; Alvarez, P.J. The Water Footprint of Biofuels: A Drink or Drive Issue? *Environ. Sci. Technol.* **2009**, *43*, 3005–3010. [CrossRef] [PubMed]
18. Hoekstra, A.Y.; Chapagain, A.K. Water footprints of nations: Water use by people as a function of their consumption pattern. *Water Resour. Manag.* **2006**, *21*, 35–48. [CrossRef]
19. Gerbens-Leenes, W.; Hoekstra, A.Y. The water footprint of sweeteners and bio-ethanol. *Environ. Int.* **2012**, *40*, 202–211. [CrossRef] [PubMed]
20. Chooyok, P.; Pumijumnog, N.; Ussawarujikulchai, A. The Water Footprint Assessment of Ethanol Production from Molasses in Kanchanaburi and Supanburi Province of Thailand. *APCBEE Procedia* **2013**, *5*, 283–287. [CrossRef]
21. Hernandes, T.A.D.; Bufon, V.B.; Seabra, J.E.A. Water footprint of biofuels in Brazil: Assessing regional differences. *Biofuels Bioprod. Biorefin.* **2014**, *8*, 241–252. [CrossRef]

22. Mathioudakis, V.; Gerbens-Leenes, P.W.; Van der Meer, T.H.; Hoekstra, A.Y. The water footprint of second-generation bioenergy: A comparison of biomass feedstocks and conversion techniques. *J. Clean. Prod.* **2017**, *148*, 571–582. [CrossRef]
23. Xie, X.; Zhang, T.; Wang, L.; Huang, Z. Regional water footprints of potential biofuel production in China. *Biotechnol. Biofuels* **2017**, *10*, 95. [CrossRef] [PubMed]
24. Wang, Y.P.; Smith, R. Wastewater minimisation. *Chem. Eng. Sci.* **1994**, *49*, 981–1006. [CrossRef]
25. Wang, Y.P.; Smith, R. Design of distributed effluent treatment systems. *Chem. Eng. Sci.* **1994**, *48*, 3127–3145. [CrossRef]
26. Zheng, P.; Feng, X.; Qian, F.; Cao, D. Water system integration of a chemical plant. *Energy Convers. Manag.* **2006**, *47*, 2470–2478. [CrossRef]
27. Alva-Argáez, A.; Kokossis, A.C.; Smith, R. The design of water-using systems in petroleum refining using a water-pinch decomposition. *Chem. Eng. J.* **2007**, *128*, 33–46. [CrossRef]
28. Mohammadnejad, S.; Bidhendi, G.R.N.; Mehrdadi, N. Water pinch analysis in oil refinery using regeneration reuse and recycling consideration. *Desalination* **2011**, *265*, 255–265. [CrossRef]
29. Tian, J.R.; Zhou, P.J.; Lv, B. A process integration approach to industrial water conservation: A case study for a Chinese steel plant. *J. Environ. Manage.* **2008**, *86*, 682–687. [CrossRef]
30. Hoekstra, A.Y.; Chapagain, A.K.; Aldaya, M.M.; Mekonnen, M.M. *The Water Footprint Assessment Manual*; Earthscan: London, UK, 2011.
31. Yan, Y.; Jia, J.; Wang, L.H.; Du, C.; Liu, X.L.; Fu, X.; Wu, G. The industrial water footprint of several typical cotton textiles in China. *Acta Ecol. Sin.* **2014**, *34*, 7119–7126. [CrossRef]
32. Agrawal, V.; Shenoy, U.V. Unified conceptual approach to targeting and design of water and hydrogen networks. *AIChE J.* **2006**, *52*, 1071–1082. [CrossRef]
33. Castro, P.; Matos, H.; Fernandes, M.C.; Nunes, C.P. Improvements for mass-exchange networks design. *Chem. Eng. Sci.* **1999**, *54*, 1649–1665. [CrossRef]
34. Yu, S.; Tao, J. Simulation-based life cycle assessment of energy efficiency of biomass-based ethanol fuel from different feedstocks in China. *Energy* **2009**, *34*, 476–484. [CrossRef]
35. Juneja, A.; Kumar, D.; Murthy, G.S. Economic feasibility and environmental life cycle assessment of ethanol production from lignocellulosic feedstock in Pacific Northwest U.S. *J. Renew. Sustain. Energy* **2013**, 5. [CrossRef]
36. Ryan, D.; Gadd, A.; Kavanagh, J.; Barton, G.W. Integrated biorefinery wastewater design. *Chem. Eng. Res. Des.* **2009**, *87*, 1261–1268. [CrossRef]
37. Jia, J.; Yan, Y.; Wang, C.; Liang, Y.; Zhang, Y.; Wu, G.; Liu, X.; Wang, L.; Du, C. The estimation and application of the water footprint in industrial processes. *Acta Ecol. Sin.* **2012**, *32*, 6558–6565. [CrossRef]
38. Mangmeechai, A.; Pavasant, P. Water Footprints of Cassava- and Molasses-Based Ethanol Production in Thailand. *Nat. Resour. Res.* **2013**, *22*, 273–282. [CrossRef]
39. Fuess, L.T.; Garcia, M.L. Anaerobic digestion of stillage to produce bioenergy in the sugarcane-to-ethanol industry. *Environ. Technol.* **2014**, *35*, 333–339. [CrossRef]
40. Mojovic, L.; Pejin, D.; Grujić, O.; Markov, S.; Pejin, J.; Rakin, M.; Vukašinović, M.; Nikolić, S.; Savić, D. Progress in the production of bioethanol on starch-based feedstocks. *Chem. Ind. Chem. Eng. Q.* **2009**, *15*, 211–226. [CrossRef]