

ENVIRONMENTAL IMPACTS OF ZERO LIQUID DISCHARGE TECHNOLOGIES

by

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Abstract

As water scarcity becomes more and more severe, to recover and reuse water in the industrial systems attracts much attention all over the world. Zero Liquid Discharge (ZLD), an ambitious industrial wastewater treatment technology, aims to eliminate any liquid waste leaving the treatment systems. The technology has been developing rapidly nowadays, raising from thermal systems to varieties of membrane systems including Reverse Osmosis, Forward Osmosis, Electrodialysis, Bipolar Electrodialysis, as well as Membrane Distillation. Considering the energy consumption, chemical inputs, and membrane uses for each system, I utilized Life Cycle Assessment (LCA) to compare the environmental performance of six ZLD systems.

I set the functional unit at 10,000 m³ feedwater treated, which reflects 4.3-91.0 hours operation of the treatment plants for current capacity in large urban centers. As a result, BMED is the most environmentally friendly ZLD technology, consuming about 34,438 kWh of electricity per functional unit, compared with 260,640 kWh for conventional thermal systems. Using coal powered electricity as the energy source, BMED ZLD systems could reduce CO₂ emissions by up to 82.1% compared with conventional thermal systems. Electricity power sources are also an influential factor for environmental impacts. Using electricity from cleaner energy power plants helps reduce CO₂ emissions and other environmental impacts. In a BMED system, the ecosystem impact of using nuclear powered electricity would be only 1.9% of that of using coal powered energy.

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Table of Contents

<i>1. Introduction</i>	<i>1</i>
<i>2. Literature Review</i>	<i>3</i>
2.1 Thermal ZLD Technology	<i>3</i>
2.2 Thermal Technology with Reverse Osmosis	<i>4</i>
2.3 Electrodialysis	<i>5</i>
2.4 Bipolar Membrane Electrodialysis.....	<i>6</i>
2.5 Forward Osmosis	<i>7</i>
2.6 Membrane Distillation.....	<i>8</i>
<i>3. Method</i>	<i>11</i>
<i>4. Results</i>	<i>12</i>
4.1 Energy Consumption.....	<i>12</i>
4.2 CO ₂ Emissions.....	<i>13</i>
4.3 Impact Assessments	<i>16</i>
<i>5. Discussion</i>	<i>19</i>
<i>6. Conclusion</i>	<i>21</i>
<i>Appendices</i>	<i>23</i>
<i>Reference</i>	<i>34</i>

1. Introduction

Due to rising water demands all over the world, freshwater scarcity becomes an essential challenge to economic growth ^[1], human health ^[2], and ecosystems conservation ^[3]. Industrial water use is one of the most important driver of freshwater consumption, which contributes to considerable amount of wastewater disposal.

In recent years, solutions for reducing industrial wastewater disposal have been raised, among which a new technology called Zero Liquid Discharge (ZLD) has attracted interests worldwide. With an ambitious wastewater treating goal, ZLD aims to eliminate any liquid waste leaving the plant, mainly the power plants, to produce clean product water for industrial reuse ^[4]. Wastewater reuse could effectively save freshwater use, alleviate the pressure of freshwater withdrawal, and reduce the environmental risk of industrial wastewater discharge. However, the environmental concerns, such as chemical use and energy consumption make the environmental performance of ZLD technologies under uncertainty.

ZLD could achieve water recovery and reuse within the industrial systems, reducing environmental risks and making the large amount of wastewater become a new resource. However, it is also related to intensive energy and material use to achieve the ambitious goal of zero discharge and has been considered not feasible and cost-effective in most cases. ^[5]

Technological research of different ZLD systems has been conducted in recent years due to more severe water scarcity and stricter regulations all over the world, such as low-salt-rejection reverse osmosis ^[6], Osmotically Assisted Reverse Osmosis ^[7], and forward osmosis ^[8]. Other ZLD technologies, such as Bipolar Membrane Electrodialysis ^[9] and Membrane Distillation ^[10], are mostly under bench scale currently. In spite of the increasing research in technical fields, the controversies of ZLD technologies have still prevailed in terms of the intensive energy and material use within the processes.

Previous studies on ZLD have limited considerations on environmental considerations, which mainly focuses on energy consumption [11-14], and thermal energy for Membrane Distillation [15]. However, a more overall environmental assessment on the whole processes of the ZLD systems is necessary. Currently, there is still a lack of research related to overall environmental impacts of ZLD technologies, which could provide important decision support for the development of ZLD.

To involve all of the processes of ZLD systems for analyzing overall environmental impacts, this research uses Life Cycle Assessment (LCA) to calculate and compare the impacts through different ZLD systems, including conventional thermal system (MVC), thermal system with Reverse Osmosis (RO), Forward Osmosis (FO), Electrodialysis (ED), Bipolar Membrane Electrodialysis (BMED), and Membrane Distillation (MD). The processes involved in the LCA mainly focus on energy consumption, chemical uses, and membrane production. Taking into account of the upstream and combustion impacts, the results of this LCA provide a comprehensive understanding of the environmental impacts of ZLD technologies.

2. Literature Review

The original brine first needs go through pretreatment, including softening, filtration, pH adjustment, anti-scalant, etc. For instance, in Seawater Reverse Osmosis (SWRO), physical (mechanical filtration) and chemical pretreatment (scale inhibitors, coagulations, disinfectants, and polyelectrolyte) are required. For a 50% recovery RO treatment, 0.1~0.2 kWh/m³ of feedwater need to be consumed. There might be post-treatment for product water as well, consuming about 0.25 kWh/m³ of feedwater^[16]. The total energy intensity for pre- and post- treatment reaches about 0.4 kWh/m³ of feedwater, which is significantly less than that of membrane and thermal stages.

2.1 Thermal ZLD Technology

To achieve zero liquid discharge, thermal processes for water vaporization are required in most of the systems. Early ZLD technologies use stand-alone thermal processes for vaporization, mainly Mechanical Vapor Compression (MVC), in a brine concentrator for the first step brine concentration, and the eventual crystallization would be realized by a brine crystallizer or an evaporation pond^[4]. The product fresh water, mainly the distillates from the brine concentrators and crystallizers in thermal systems, would be reused by the industrial system, and the solids can be reused or sold as byproducts (Fig. 1). Thermal systems set a benchmark for ZLD membrane based technologies, promoting the efforts towards higher energy efficiency to reduce environmental impacts. Evaporation ponds, an alternative of brine crystallizer, could utilize natural solar energy instead of electricity.

According to studies for ZLD application in water utilities and drinking water systems, the energy intensity for brine concentrator varies from 18.5 to 26.4 kWh/m³ feedwater^[17-18], and brine crystallizer consumes 52.8~66.0 kWh/m³ feedwater. The water recovery from concentrators reaches about 90~98%, thus about 2~10% of the wastewater feeds into the

crystallizer. Total energy consumption for one functional unit (10,000 m³ feedwater) leads to 260,640 kWh of electricity.

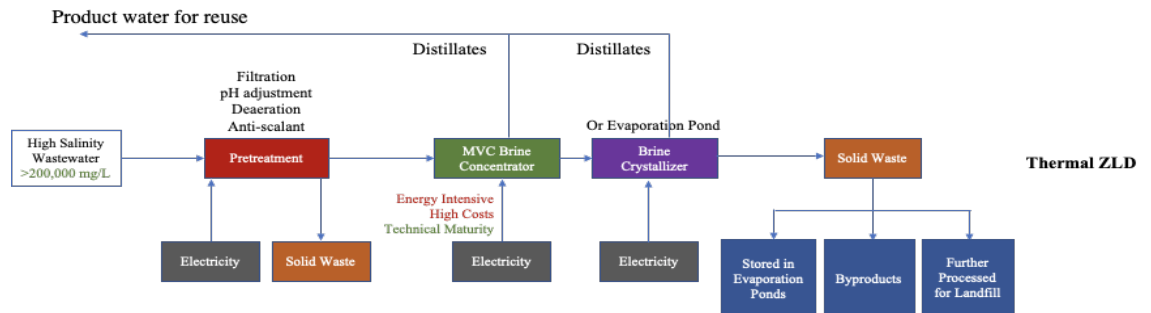


Fig. 1 Thermal ZLD Technology Diagram

2.2 Thermal Technology with Reverse Osmosis

Efforts have been focused on reducing the brine volume entering the crystallizer since the final evaporation step (crystallizer or evaporation pond) is indispensable currently in ZLD systems. Reverse Osmosis technology involves a membrane system before thermal stages to reduce the brine volume going to the concentrators. The pretreatments, including softening, filtration, and pH adjustment, requires intense use of chemicals like Hydrated lime, soda ash, silica, and anti-scalant, to reduce scaling potential of RO membrane. The extensive pretreatment results in additional solid waste.^[19] The product water for reuse comes from the permeate of RO and the distillates of brine concentrator and crystallizer.

RO has high potential of membrane scaling, thus the wastewater treated has a limited salinity concentration^[20], for which the limit TDS of the feedwater is less than 75,000 mg/L. The RO system is more energy efficient than conventional MVC systems because the RO processes reduce the water volume entering both the energy intensive brine concentrator and brine crystallizer. RO requires 2 stages of RO membranes (Fig. 2). According to inland desalination data, the primary RO could reach a 75%-85% recovery, while the combined recovery of the two RO stages reaches 92.5%-95.5%^[21].

For the energy consumption, an SWRO membrane system of a 50% water recovery has the energy intensity of 0.9 kWh/m³ [22-23]. While the rest 50% of the feedwater would continue going into the thermal stages of brine concentrator and crystallizer. Therefore, the total energy consumption for a functional unit is about 139,320 kWh of electricity.

The chemicals used for SWRO are in four phases: extraction, pretreatment, RO membrane, and post-treatment, including sodium hypochlorite, citric acid, caustic soda, lime, carbon dioxide, and chlorine, etc. [24] The use of pretreatment chemicals mainly aims to clean membranes and remove chlorine.

The water salinity concentrations (TDS) of brackish water ranges between 1,000 and 8,000 mg/L, while that of seawater is around 35,000 mg/L [25]. Therefore, Brackish Water Reverse Osmosis (BWRO) would cost less than SWRO. For a 92.5~95.5% water recovery in BWRO, the membrane stage consumes 1.4~2.4 kWh/m³ feedwater [12][21]. The rest 4.5~7.5% of feedwater goes to the next thermal stages, including brine concentrators and crystallizers, thus the total energy consumption is about 34,438 kWh per functional unit.

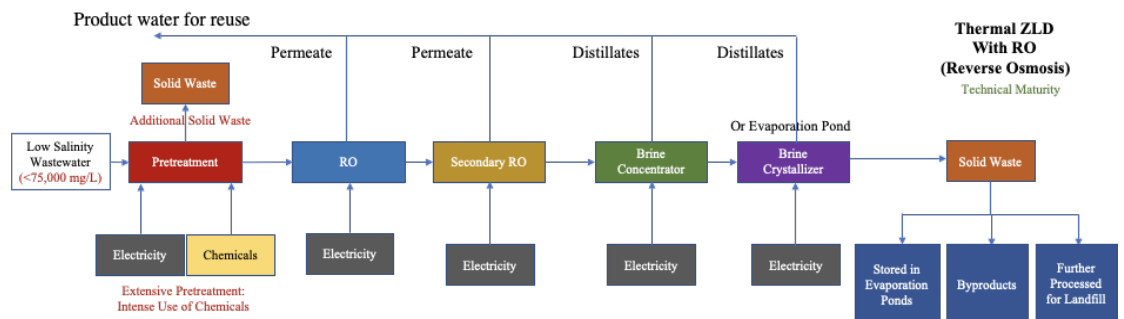


Fig. 2 RO ZLD Technology Diagram

2.3 Electrodialysis

The Electrodialysis or Electrodialysis Reverse (ED/EDR) system is to replace the secondary RO process with electrodialysis membrane, which reduces the membrane scaling potential. With low scaling propensity, the

ED/EDR system is able to treat high salinity wastewater with an upper concentration (TDS) higher than 100,000 mg/L. Other processes remaining similar, the pretreatment before the ED/EDR membrane requires less chemicals, which reduces solid waste compared with RO systems (Fig. 3) [21].

According to multiple research discussing Electrodialysis systems for ZLD applications, the water recovery at the membrane stage is about 77~98%, while the energy intensity ranges between 7.0 and 17.0 kWh/m³ feed water [26-29]. Considering the membrane and thermal stages, total energy consumption for ED systems is about 153,883 kWh per functional unit.

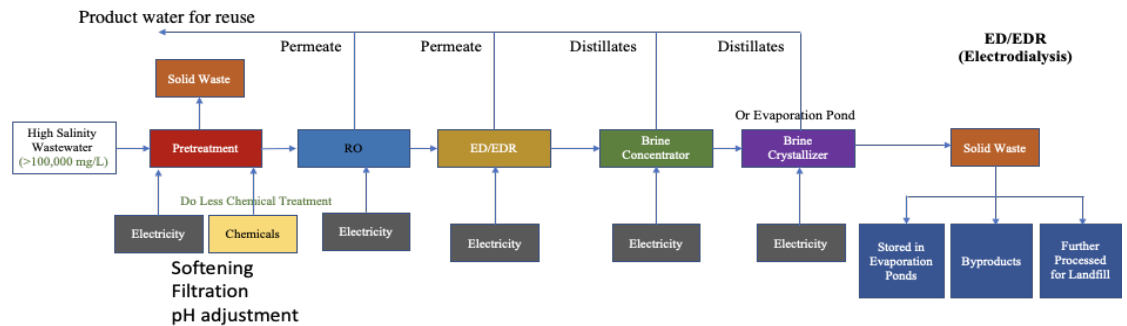


Fig. 3 ED/EDR ZLD Technology Diagram

2.4 Bipolar Membrane Electrodialysis

As a variant of the ED system, BMED uses one bipolar membrane (BM) between each anion exchange membrane (AEM) and cation exchange membrane (CEM) to form a CEM/BM/AEM assembly. Without any thermal processes, BMED generates strong acids and bases as byproducts which can be directly used in some industries (Fig. 4), making the system more cost-effective [9].

Currently, BMED is still at bench scale, without treatment applications. According to the laboratory data for glyphosate recovery, when at the current density of 40 mA/cm², the energy intensity of BMED is about 2.7 kWh/kg NaOH produced [9]. Therefore, the total energy consumption when treating one functional unit feedwater is about 46,400 kWh of electricity.

In a pellet reactor of BMED, the reagents used in the experiments include H_2SO_4 97%, HNO_3 56%, HCl , NaOH , Na_2CO_3 , Na_2SO_4 , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, etc., to pretreat the ions in the industrial wastewater including calcium, nickel, sodium, strontium, iron, chromium, and sulfate [30]. BMED leads to higher membrane consumption than conventional ED because a bipolar membrane is required between the AEM and CEM, such as FKB, FAB, and FMB membrane systems in the reactor, with the thickness of 0.1~0.12 mm, 0.09~0.11 mm, and 0.18~0.2 mm respectively.

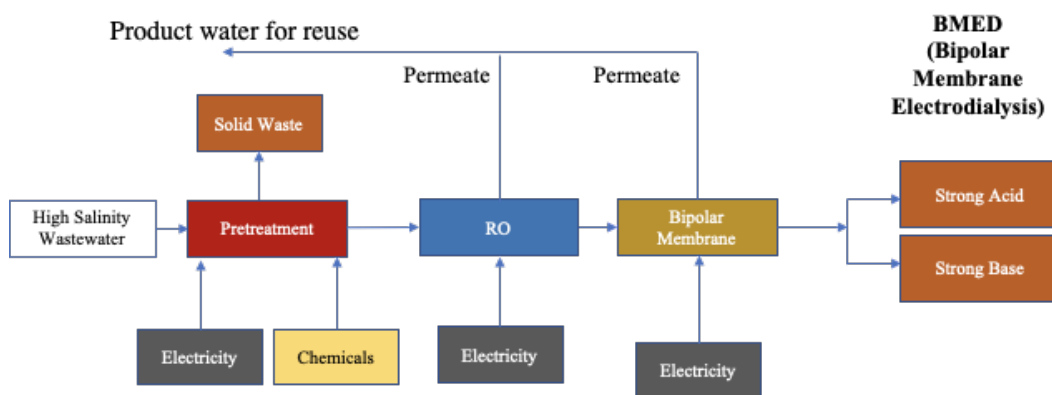


Fig. 4 BMED ZLD Technology Diagram

2.5 Forward Osmosis

FO membrane also has a low scaling propensity; thus, it can treat high salinity wastewater whose upper concentration is higher than 200,000 mg/L. There is no softening pretreatment before the FO membrane. With FO membrane, the system could reach similar recovery as secondary RO without using chemicals, also reducing the solid waste compared with RO systems [21].

In FO systems, the thermolytic NH_3/CO_2 draw solution can give high osmotic pressure-driving force for fresh water absorbing and brine concentrating. After the dilution of the draw solution, low grade energy can be utilized to regenerate the concentrated solution because it can decompose at moderate temperature (Fig. 5).

However, an FO-RO system is still more energy-intensive than a RO system [31]. To produce product water for reuse, another RO or distillation process is required to extract the water from the diluted solution in the membrane systems, contributing more energy consumption, because the product water in the FO process cannot be directly separated but go into the concentrated draw solution.

Therefore, FO becomes the most electricity consuming membrane technology among all of the six systems, only less than the thermal ZLD method. According to a pilot demonstration, FO systems consume about 210,000 kWh of electricity per functional unit.

The chemical used in FO systems is mainly sodium chloride as the solute of the draw solution. The amount of chemical input depends on low or high permeability for the FO membranes as well as the draw solution concentration (g/L). For the average data of 20, 30, 40, and 50 g/L draw solution concentration, 3.01 t of sodium chloride is required for low permeability membrane, and 1.95 t is required for high permeability [32] one for one functional unit of feedwater treatment. A RO membrane stage follows after the FO stage, which consumes about 2.11 t of sodium chloride for one functional unit.

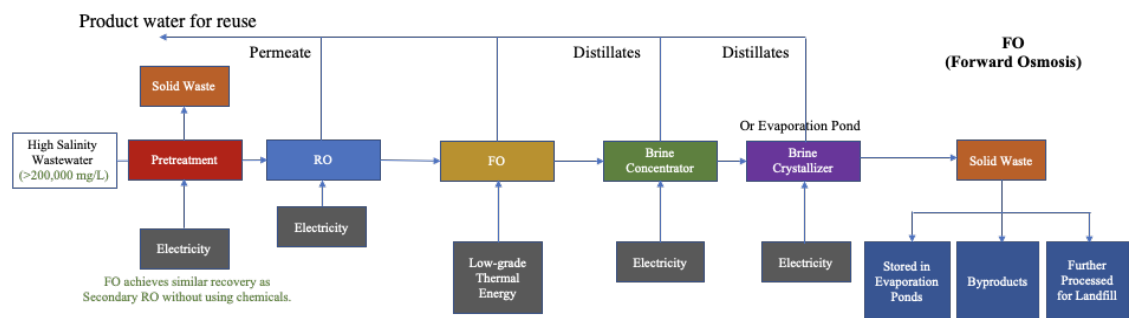


Fig. 5 FO ZLD Technology Diagram

2.6 Membrane Distillation

Similar to BMED, Membrane Distillation is also still at bench scale, which could treat high salinity wastewater and has low scaling propensity. It

can also utilize low-grade thermal energy, like FO, but MD has low water recovery and flux ^[21]. Liquid-vapor phase transition is required for water separation and MD would consume more energy compared with RO and ED systems ^[33]. If volatile pollutants are present, post-treatment is needed because MD membrane has potential of membrane wetting (Fig. 6).

Direct Contact Membrane Distillation (DCMD) and Air Gap Membrane Distillation (AGMD) are two types of MD technologies. In DCMD systems, liquid phases are in direct contact with the two sides of the membranes. At an 80% water recovery DCMD system, the energy intensity at the membrane stage is about 39.7~45.0 kWh/m³ feedwater, but differently, low-grade energy (e.g. geothermal) could be used at this stage, meaning that 424,000 kWh of thermal energy would be consumed for per functional unit feedwater treated. The following thermal stages, including brine concentrator and crystallizer, lead to about 52,128 kWh of electricity consumed for the same unit.

At AGMD systems, only the feed brine is in direct contact with the membrane on one side, while the permeate would be condensed on the other side. For a 50% water recovery at the AGMD membrane, the thermal energy intensity at the membrane stage is about 22.2~66.7 kWh/m³ feedwater, therefore 445,000 kWh of thermal energy would be consumed for one functional unit feedwater treated. The following thermal stages would consume about 130,320 kWh of electricity for one functional unit feedwater treatment.

There are five chemical pretreatment phases for MD systems, using NaOH, Na₂CO₃, and BaCl₂ to remove calcium, carbonic species, and sulfate in the feed water, as well as neutralizing the carbonic acid and adjusting pH ^[34]. Polytetrafluoroethylene (PTFE) flat sheet membranes (TF 200 and TF 450) supported by a polypropylene (PP) net were used in the systems as the main membrane ^[34].

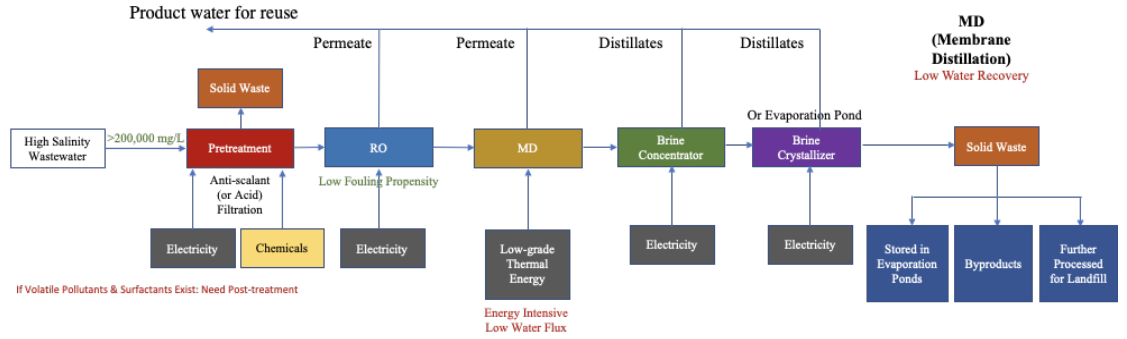


Fig. 6 MD ZLD Technology Diagram

Current research each focuses mainly on a single aspect of ZLD systems, such as electricity consumption or technical details, but lacks the overall environmental analysis of different ZLD systems' life cycle assessments. The goal of this research is to compare different ZLD technologies in a whole sight of environmental impacts, including energy consumption, carbon emissions, human health impacts, ecosystem impacts, and resource impacts, etc., as well as exploring how different ZLD technologies and energy sources determine the environmental performances.

3. Method

To comprehensively assess the environmental impacts of different ZLD systems, this research implements Life Cycle Assessment (LCA) for data calculation. LCA is an analysis technique to analyze environmental impacts associated with all the stages of a product's life from upstream material extraction through processing, manufacturing, distribution, use, and end-of-life.

Using LCA, all of the energy consumption and material inputs can be translated into impact assessments, including human health, ecosystems, and resources, which makes the comparison between different technologies possible. Besides different ZLD technologies, this research also compares the environmental impacts between different energy sources, including coal, industrial gas, nuclear, solar, wind, and biomass generated electricity.

For the scope definition, the functional unit for LCA calculation is 10,000 m³ feedwater. In recent coal-to-chemical industries in China, the treatment capacity ranges widely from 110 to 2,300 m³ feedwater per hour^[35-38]. The functional unit of 10,000 m³ feedwater reflects 4.3-91.0 hours operation of the treatment plants. The LCA calculation was realized by SimaPro, a model builder and systematic LCA analyzer, through the data of energy consumption, chemical inputs, and membrane uses gathered from previous research of different ZLD systems.

In SimaPro, analyze calculation and ReCiPe 2016 Endpoint method were implemented for all of the energy sources and ZLD technologies. Other settings can be found at Table. 1.

Table. 1 SimaPro Settings

Calculation:	Results:	Product:	Method:	Indicator:
Analyze	Impact assessment	1 p ED (of project ZLD)	ReCiPe 2016 Endpoint € V1.03 / World (2010) E/A	Characterization
Skip categories:	Exclude infrastructure processes:	Exclude long-term emissions:	Sorted on item:	Sort order:
Never	No	No	Impact category	Ascending

4. Results

4.1 Energy Consumption

Among all of the 6 ZLD technologies, the conventional thermal MVC system is most energy intensive, which is why other new membrane-based technologies emerged. Based mostly on evaporation and distillation, thermal MVC technology consumes about 260,640 kWh^[39-40] of electricity for brine concentrator and crystallizer for one functional unit, which is 10,000 m³ of feedwater. Forward Osmosis (FO) ZLD technology is also quite energy intensive, which consumes about 210,000 kWh^[41] electricity per functional unit, over 80.57% of the electricity consumption of conventional thermal systems. The main reason is the large amount of energy consumption for separating product water from the draw solution, which could be a necessary post treatment for freshwater reuse^[42]. The following ones of energy intensity are Electrodialysis/Electrodialysis Reverse (ED/EDR), Seawater Reverse Osmosis (SWRO), and Membrane Distillation (MD). The total energy amount that MD ZLD systems consume could be larger, but MD systems could use low-grade energy sources, such as geothermal energy, and the electricity consumed would be reduced. The most energy saving technology is Bipolar Electrodialysis (BMED), consuming 34,438 kWh^{[21][12]} of electricity per functional unit, which is only 13.21% of the amount MVC systems use (Table. 2; Fig. 7). Currently, MD and BMED systems are mostly at bench scale, meaning that future possible industrial application could be to some extent more energy saving than the date below.

Table. 2 Electricity Consumption of 6 ZLD Technologies

Technology	MVC	FO	ED	SWRO	MD	BMED
Electricity (Unit: kWh/Functional Unit)	260,640	210,000	153,883	139,320	91,224	34,438

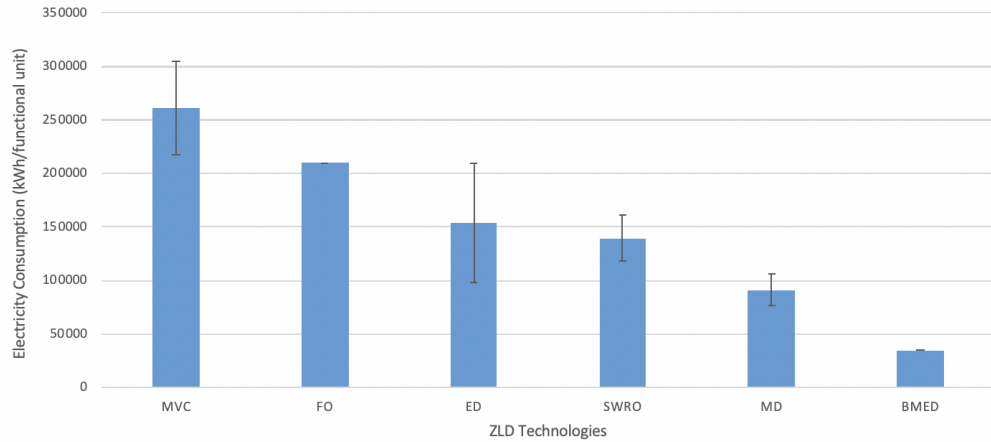


Fig. 7 Electricity Consumptions of 6 ZLD Technologies

4.2 CO₂ Emissions

SimaPro allows the calculation and summary of airborne emissions and I mainly care about carbon dioxide emissions at this research. The total CO₂ emissions consist of fossil, biogenic, and land transformation CO₂. Carbon dioxide emission is highly related to energy source types, so I switched different energy sources generated electricity between coal, industrial gas, nuclear, solar, wind, and biomass and compared different CO₂ emissions.

CO₂ emissions are mostly determined by electricity generation, for the reason that power plants are the most important source of carbon emissions among the systems. For different energy generation methods, the chemical and membrane inputs remain the same, so the comparisons between the energy sources types are similar among all the 6 ZLD technologies.

Taking the most energy saving technology, BMED, as an example, coal generated electricity leads to most carbon emissions, about 160,050 kg CO₂ in total (including the impacts by the chemicals and membranes) per functional unit. Biomass and industrial gas generated energy are also intensive at CO₂ emissions, which are 41,815 kg and 34,677 kg respectively. Solar, wind, and nuclear energy are relatively cleaner. If using nuclear energy, the BMED ZLD system only generates 1,077 kg CO₂ emissions per

functional unit, which is only 0.67% of the emissions when using coal as the power source (Fig. 8).

Comparing the 6 ZLD technologies assuming that coal is the only energy source generating electricity, the most energy intensive conventional thermal MVC system causes 894,156 kg CO₂ emissions, which is about 5.6 times of BMED system emissions. Other technologies, including FO, ED, SWRO, and MD, lead to 721,148 kg, 529,113 kg, 479,111 kg, and 392,484 kg of CO₂ emissions respectively. The ranks of carbon emissions of the 6 energy sources should remain consistent among different ZLD technologies. Similarly, the ranks between different ZLD technologies should remain the same when controlling the energy source.

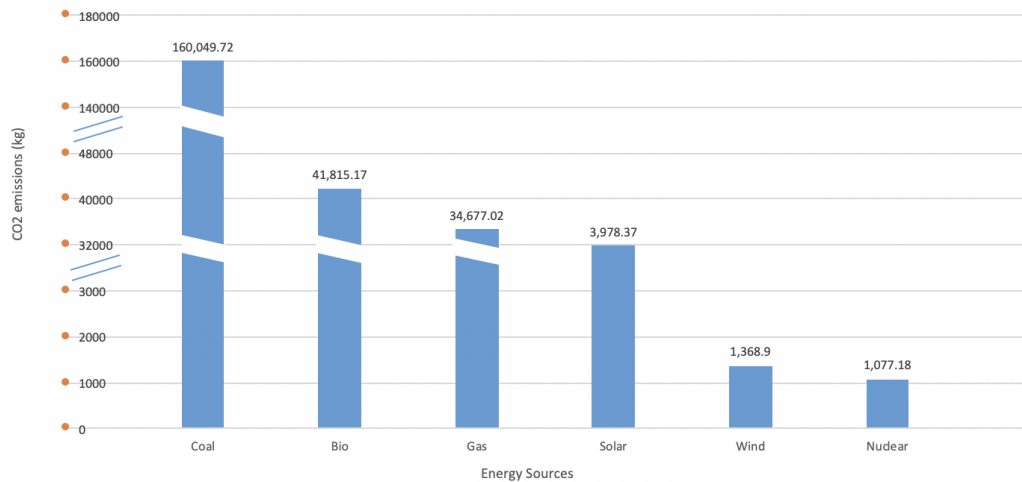


Fig. 8 CO₂ Emission of 6 Energy Sources for BMED Systems

When comparing CO₂ emissions for the same energy source between the 6 ZLD technologies, taking coal as an example energy source, the rank of the technologies is consistent with that of the electricity consumption owing to the fact that energy contributes most of the impacts when considering life cycle environmental performances, while the chemicals and membrane only contributes tiny portions of impacts especially when using coal as the energy source. Thermal ZLD systems would lead to 894,156 kg of CO₂ for one

functional unit feed water treated, while BMED systems would only cause about 17.90% of thermal carbon emissions, 160,050 kg CO₂ (Fig. 9).

However, taking nuclear energy as another instance, because there would be much less electricity related CO₂ emissions, chemicals and membranes play a more important role in carbon emission impacts. Therefore, the rank of the 6 ZLD technologies changed: Membrane Distillation became the most carbon intensive system because of the large amount of chemical inputs at the chemical pretreatment phases. Thermal systems became much more environment friendly because their chemical inputs are much less than the membrane ones. MD counts for 79,534 kg CO₂ emissions per functional unit, which is significantly more than other 5 systems, compared with that thermal systems counts for 1,819 kg and BMED counts for only 1,077 kg for one functional unit feedwater treated (Fig. 10). Therefore, energy sources have an important influence on the environmental performance comparison of different systems due to the different impact portions of the energy, chemical, and membrane parts.

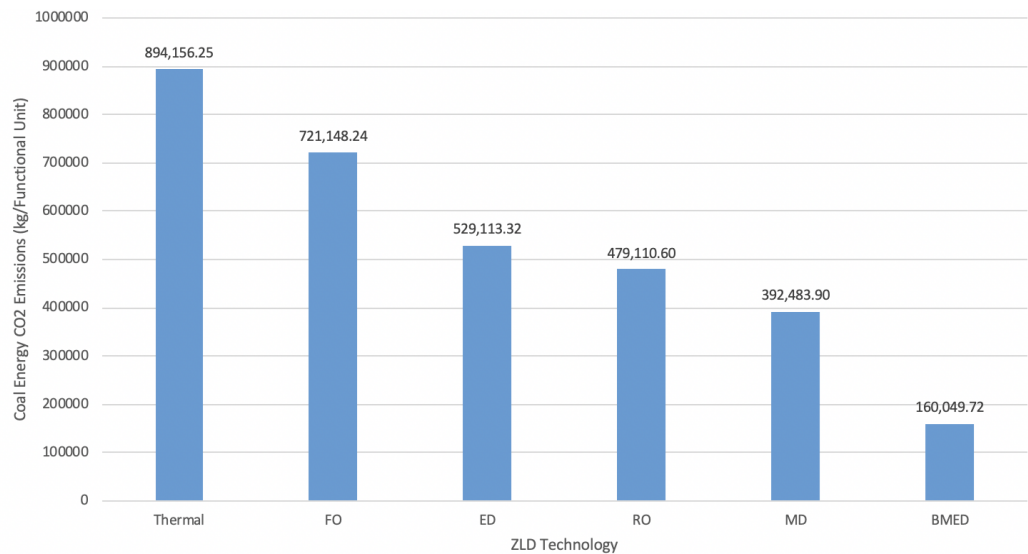


Fig. 9 Coal Energy Source CO₂ Emissions for 6 ZLD Technologies

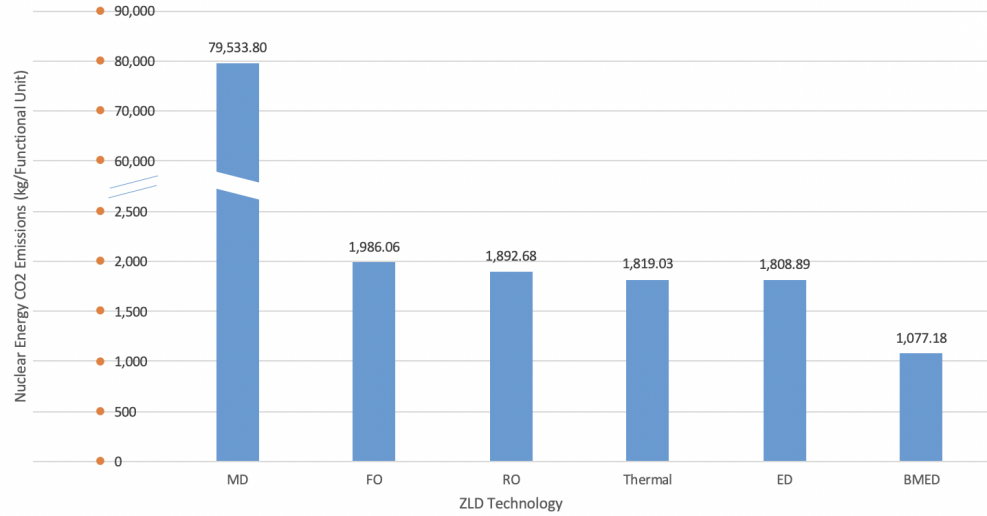


Fig. 10 Nuclear Energy Source CO₂ Emissions for 6 ZLD Technologies

4.3 Impact Assessments

SimaPro provides three types of Impact Assessments, including human health, ecosystems, and resources. For BMED systems, coal generated electricity contributes more than 99.2% of the human health and ecosystems impacts, and more than 98.5% of the resources impacts. By comparison, nuclear energy contributes 61.0%, 60.2%, and 42.8% of the impacts respectively, and biomass generated energy contributes 37.2%, 74.1%, and 23.5%.

In BMED ZLD systems, coal generated energy causes 7.77 DALY of human health impact, which is more than 88 times of the biomass generated energy’s impact, 0.088 DALY. Gas, solar, wind, and nuclear power lead to 2.68, 1.15, 0.20, and 0.14 DALY respectively. Wind, nuclear, and biomass energy have significantly less human health impacts than the other three (Fig. 11).

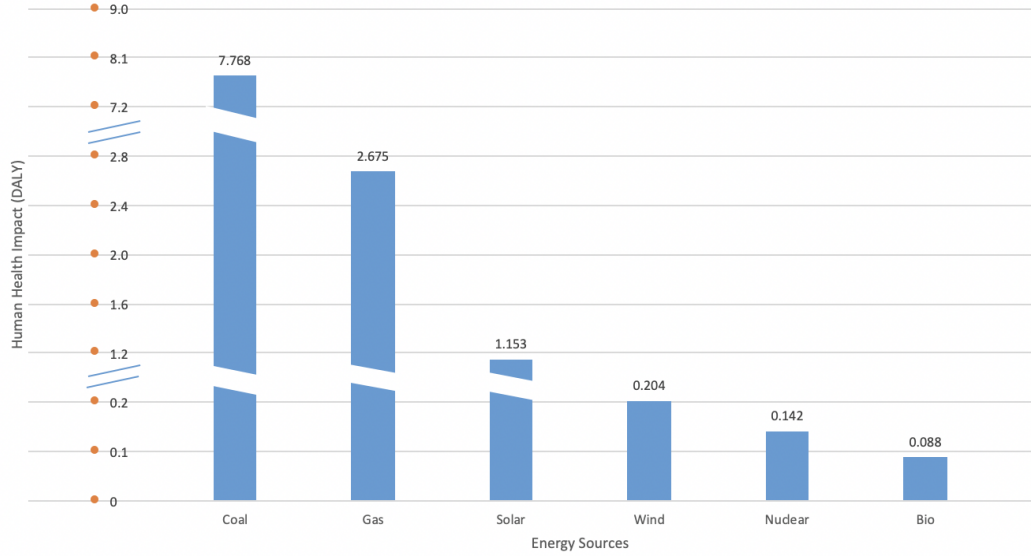


Fig. 11 Human Health Impact Assessment of BMED Systems

Similarly, coal generated energy leads to most impacts on ecosystems, which is $6.69E-03$ species.yr per functional unit. Nuclear energy contributes to the least impact on ecosystems, $1.3E-04$ species.yr. Coal, industrial gas, and solar energy have significantly larger ecosystems impacts than biomass, wind, and nuclear power (Fig. 12). The ecosystem impact of the BMED system when using nuclear electricity is less than 2% of that when using coal energy.

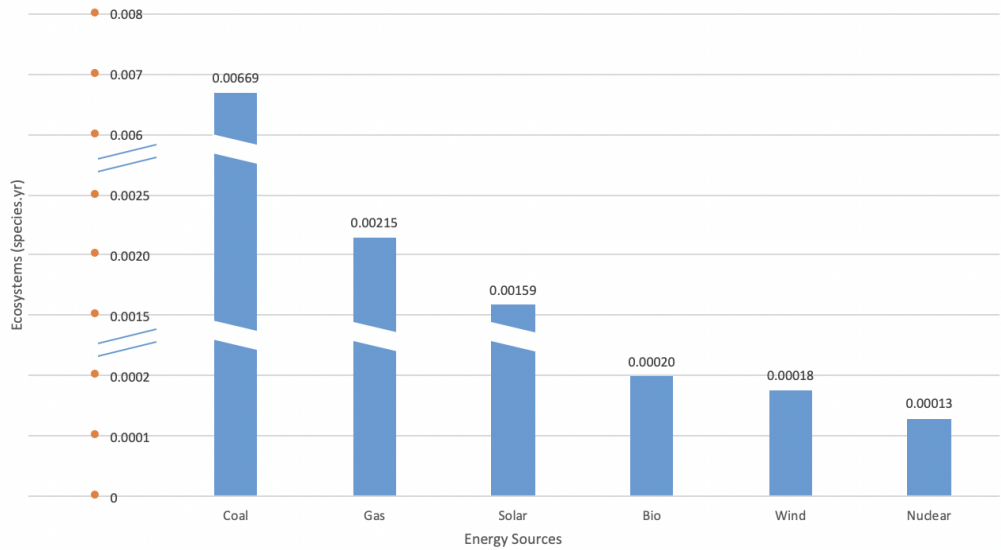


Fig. 12 Ecosystems Impact Assessment of BMED Systems

For resource impacts, coal energy also has the most impact among all of the 6 energy sources, 3,526.9 USD2013. The BMED systems when using biomass energy remain the lowest impact, 65.4 USD2013, which is less than 2% of that consuming coal energy (Fig. 13). The systems using nuclear and wind energy also have low impacts on resources, which are respectively 87.5 and 111.9 USD2013.

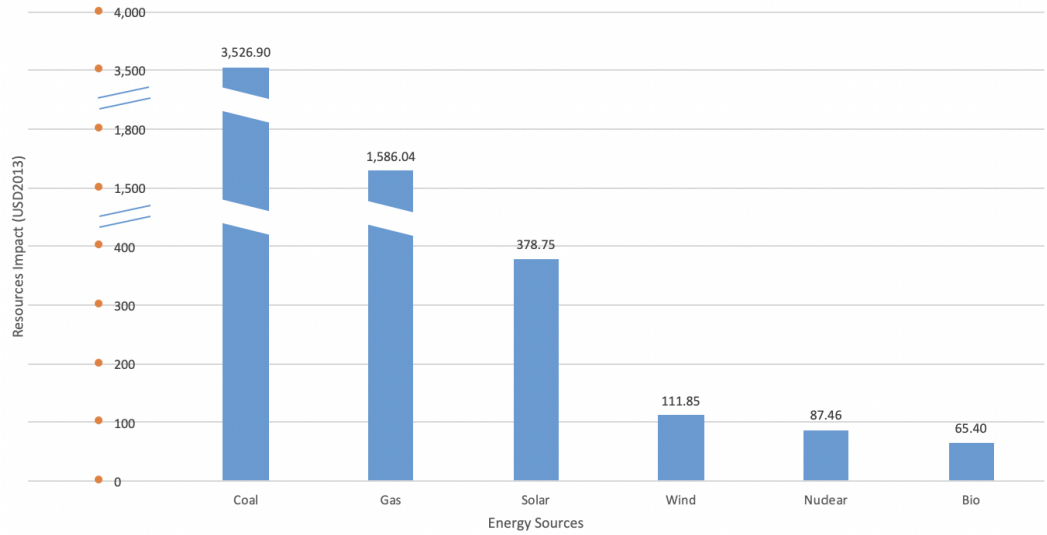


Fig. 13 Resources Impact Assessment of BMED Systems

5. Discussion

Based on SimaPro LCA calculations, energy consumption, carbon emissions, and impact assessments were analyzed between 6 ZLD technologies and 6 different energy sources. However, the original data inputting into the software was from varieties of desalination and industrial wastewater treatment research. Because of the different types of industrial wastewater, the treatments of the 6 technologies were very different. The chemical inputs are mostly at the pretreatment stage to roughly remove some specific ions within the feedwater, like Ca^{2+} and Mg^{2+} . However, due to the different wastewater components and TDS, the chemical uses for pretreatment were to some extent different across the 6 systems. For instance, the chemical inputs for SWRO were for seawater desalination in western Australia^[43]. The SWRO brine was supplied by the company Abengoa Water S.L.U., corresponding to the brine discharged by a desalination plant located in Almería (Spain)^[42].

As for the energy consumption data, because of the lack of specific pretreatment energy intensity for each technology, I only counted for the energy involving in the membrane stages and thermal stages, without the pretreatment related consumption due to the fact that pretreatment energy is much less than that consumed in the following stages. The energy consumption data comes from the average amount regarding the data range from plenty of research, and the error bars were calculated from the upper and lower limit of the range.

Remarkably, I failed to find the chemical use data for ED and BMED but got the information that these two systems were similar, and ED uses a little less chemical than SWRO technology. Therefore, I took the same chemical use types of SWRO for ED and BMED and set 80% of the amount for each one. Also missing the chemical data of thermal MVC systems, I ignored the chemical uses for thermal technology, because it would be significantly less than other membrane methods. For membrane data, I took polyamide as the material for all membranes, changing the amount of the

plastic based on the ratio of the membrane area to be replaced for a functional unit^[44]. However, the processing and manufacturing of membranes would be missed if only consider the plastic materials.

In addition, some of the technologies are still at bench scale, such as BMED and MD, so I used the laboratory data to compare with the pilot or application data of other systems, which could be inaccurate in data comparison. Data accuracy of this research could be further improved in terms of the aspects mentioned above. When it comes to the two types of RO, SWRO and BWRO, the energy and chemical use difference mainly results from the different TDS of the feed brine, therefore, I chose SWRO as a more typical type for RO calculation in the life cycle assessments.

Besides energy, chemicals, and membranes, there are also other aspects that could be considered into the calculation, such as solid waste treatment, other gas emissions, and more details of different membrane material uses. More aspects consideration should add to the total impacts and emissions of the systems. Future study could focus on the improvement of data, such as detailed chemical and membrane inputs, to give key specific recommendations for ZLD applications.

6. Conclusion

Among all of the 6 ZLD technologies, Bipolar Membrane Electrodialysis is overall the most environmentally friendly system, consuming 34,438 kWh electricity for one functional unit feedwater treatment, compared with the most energy consuming one, conventional thermal ZLD systems, which contributes to 260,640 kWh electricity consumption. Forward Osmosis, Electrodialysis, Reverse Osmosis, and Membrane Distillation are other membrane technologies that are more energy saving than thermal systems, counting for 210,000 kWh, 153,883 kWh, 139,320 kWh, and 91,224 kWh respectively per functional unit.

Remarkably, the electricity power sources are an essential factor when comparing the overall environmental impacts of the technologies, including CO₂ emissions, human health, ecosystems, and resources. Using fossil fuels including coal and industrial gas as the energy sources, electricity consumption contributes most of the environmental impacts compared with chemical inputs and membrane uses. Therefore, conventional thermal ZLD systems lead to most CO₂ emissions when using coal as power source, while Membrane Distillation became the most CO₂ intensive one when considering switching the energy source to nuclear, because chemical inputs stand out when the electricity power plants become cleaner.

Looking at the most environmentally friendly ZLD system example - Bipolar Membrane Electrodialysis, coal power causes most CO₂ emission, about 160,050 kg per functional unit, while nuclear energy remains the cleanest source, leading to 1,077 kg, which is only 0.67% of thermal systems. Besides, wind and solar are also CO₂ reducing sources, leading to 1,369 kg and 3,978 kg CO₂ emissions respectively. As the technology of the least environmental impact, BMED also remains the least carbon emissions from coal power to nuclear power.

LCA impact assessment includes human health, ecosystem, and resource parts, among which biomass power source remains the lowest impact for human health and resources, while nuclear plants have the least

impacts on ecosystems. Nuclear, wind, and biomass maintain the three lowest environmental impacts for all of the three parts, while solar always contributes the highest impacts among all of the non-fossil fuels. Coal and industrial gas remain the largest environmental impacts for all of the three parts including human health, ecosystems, and resources.

To better improve the application of ZLD technologies and reduce the overall environmental impacts, using membrane systems instead of only utilizing thermal stages is essential for saving energy consumption. Among all of the membrane technologies, Bipolar Membrane Electrodialysis is the most environmentally friendly one, although it's still at bench scale and not going into pilot and application stage yet. Besides the choices of technologies, electricity power source is also a vital factor to be considered for reducing environmental impacts. Using the electricity from cleaner power plants could reduce as much as 98% of the environmental impacts.

Appendices

Stage	Energy Intensity (kWh/m ³)	Energy Intensity for Calculation (kWh/m ³)	Percent of the feedwater from last stage	Percentage for Calculation	Energy Consumption (kWh/Functional Unit)	Total (kWh/Functional Unit)
Brine Concentrator	18.5~26.4	22.5	100%	100%	225,000	260,640
Brine Crystallizer	52.8~66.0	59.4	2~10%	6%	35,640	

Energy Consumption of Thermal ZLD Systems

Water Recovery in SWRO: 50%

Stage	Energy Intensity (kWh/m ³)	Energy Intensity for Calculation (kWh/m ³)	Percent of the feedwater from last stage	Percentage for Use	Energy Consumption (kWh/Functional Unit)	Total (kWh/Functional Unit)
SWRO	0.9	0.9	100%	100%	9,000	139,320
Brine Concentrator	18.5~26.4	22.5	50%	50%	112,500	
Brine Crystallizer	52.8~66.0	59.4	2~10%	6%	17,820	

Energy Consumption of Thermal ZLD With SWRO Systems

Water Recovery in BWRO:92.5~95.5%

Stage	Energy Intensity (kWh/m ³)	Energy Intensity for Calculation (kWh/m ³)	Percent of the feedwater from last stage	Percentage for Use	Energy Consumption (kWh/Functional Unit)	Total (kWh/Functional Unit)
BWRO	1.41~2.35	1.88	100%	100%	18,800	34,438
Brine Concentrator	18.5~26.4	22.5	4.5~7.5%	6%	13,500	
Brine Crystallizer	52.8~66.0	59.4	2~10%	6%	2,138	

Energy Consumption of Thermal ZLD With BWRO Systems

Stage	Energy Intensity (kWh/m ³)	Energy Intensity for Calculation (kWh/m ³)	Percent of the feedwater from last stage	Percentage for Use	Energy Consumption (kWh/Functional Unit)	Total (kWh/Functional Unit)
ED/EDR	7~17	12	100%	100%	120,000	153,883
Brine Concentrator	18.5~26.4	22.5	2~23%	13%	29,250	
Brine Crystallizer	52.8~66.0	59.4	2~10%	6%	4,633	

Energy Consumption of ED/EDR Systems

Stage	Energy Intensity (kWh/m ³)	Total Energy Consumption (kWh/Functional Unit)
Overall FO System	21	210,000

Energy Consumption of FO Systems

Stage	Energy Intensity	Energy Intensity for Calculation (kWh/m ³)	Percent of the feedwater from last stage	Percentage for Use	Energy Consumption (kWh /Functional Unit)	Total Energy/ Functional Unit
DCMD	39.7~45 (kWh/m ³)	42.4 (kWh/m ³)	100%	100%	424,000	424,000 (Thermal)
Brine Concentrator	18.5~26.4 (kWh/m ³)	22.5 (kWh/m ³)	20%	20%	45,000	52,128 (Electricity)
Brine Crystallizer	52.8~66.0 (kWh/m ³)	59.4 (kWh/m ³)	2~10%	6%	7,128	

Energy Consumption of DCMD Systems

Stage	Energy Intensity	Energy Intensity for Calculation (kWh/m ³)	Percent of the feedwater from last stage	Percentage for Use	Energy Consumption (kWh /Functional Unit)	Total Energy /Functional Unit
AGMD	22.2~66.7 (kWh/m ³)	44.5 (kWh/m ³)	100%	100%	445,000	445,000 (Thermal)
Brine Concentrator	18.5~26.4 (kWh/m ³)	22.5 (kWh/m ³)	50%	50%	112,500	130,320 (Electricity)
Brine Crystallizer	52.8~66.0 (kWh/m ³)	59.4 (kWh/m ³)	2~10%	6%	17,820	

Energy Consumption of AGMD Systems

Stage	Current Density (mA/cm ²)	Operation Time (min)	Fluid Flow Rate (L/h)	Energy Intensity (kWh/kg NaOH)	Final Volume of NaOH (L)	Final Concentration of NaOH (mol/L)	Water Volume (L)	NaOH (kg)	Energy Consumption (kWh)	Total Energy (kWh/Functional Unit)
Overall BMED	40	90	100	2.7	2.8	2.3	150	0.2576	0.6955	46,400

Energy Consumption of BMED Systems

Phase	Inputs	Amount (of product water)	Amount (of feedwater)	Unit	For Functional Unit	Unit
Extraction	Sodium Hypochlorite	1.94E-03	1.82E-03	l/m ³	18.2	l
Pretreatment	Membrane	290	272.6	g/m ³	2.726	t
	Sodium Hypochlorite	1.63	1.5322	g/m ³	15.322	kg
	Sulfuric Acid	0.686	0.64484	g/m ³	6.4484	kg
	Citric Acid	0.282	0.26508	g/m ³	2.6508	kg
	Sodium Metabisulphite	0.0739	0.069466	g/m ³	694.66	g
RO	Nalco PC1020	3.06	2.8764	g/m ³	28.764	kg
	Citric Acid	0.655	0.6157	g/m ³	6.157	kg
	Detergent	2.72E-03	0.0025568	l/m ³	25.568	L
	DBNPA	6.79E-03	0.0063826	l/m ³	63.826	L
	Caustic Soda	3.60E-02	0.03384	l/m ³	338.4	L
	Membrane (1st pass)	34.00	31.96	g/m ³	319.6	kg
Membrane (2nd pass)	2.00	1.88	g/m ³	18.8	kg	
Post-treatment	Lime	51.03	47.97	g/m ³	479.7	kg
	Carbon dioxide	43.00	40.42	g/m ³	404.2	kg
	Chlorine	1.200	1.13	g/m ³	11.3	kg
	Fluorosilicic acid	0.85	0.80	g/m ³	8.0	kg
	Polyelectrolyte	0.03	0.03	g/m ³	0.3	kg

Chemical Use of SWRO Systems

Water Recovery: 64%

Phase	Draw Solution Concentration (g/L)	Chemical	Use of product water (g/m ³)	Use of feedwater (g/m ³)	Average Chemical Inputs (g/m ³)	For Functional Unit (t)
Low permeability membrane FO	20	Sodium Chloride	640	409.6	300.8	3.008
	30	Sodium Chloride	490	313.6		
	40	Sodium Chloride	400	256		
	50	Sodium Chloride	350	224		
High permeability membrane FO	20	Sodium Chloride	400	256	195.04	1.9504
	30	Sodium Chloride	329	210.56		
	40	Sodium Chloride	260	166.4		
	50	Sodium Chloride	230	147.2		
RO	20	Sodium Chloride	100	64	211.2	2.112
	30	Sodium Chloride	230	147.2		
	40	Sodium Chloride	490	313.6		
	50	Sodium Chloride	500	320		

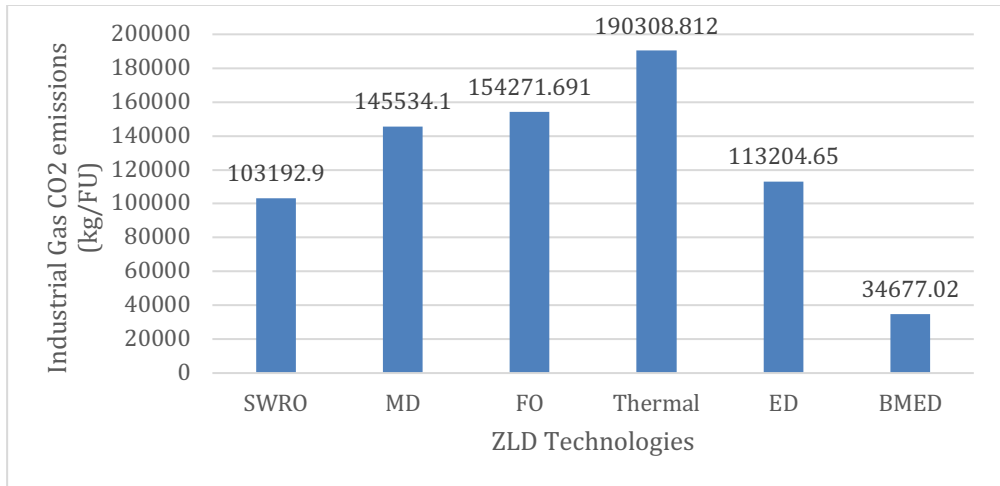
Chemical Use of FO Systems

Pretreatment Phases	Chemical	Objectives
Chemical Pretreatment 1	NaOH	Remove the temporary calcium hardness (carbonate calcium hardness); Neutralize the carbonic acid; Remove the carbonic species in the RO brine which may react with calcium ions to form CaCO ₃ . 0.4g/L NaOH solution (After this phase, the pH is 7.9)
Chemical pretreatment 2	Na ₂ CO ₃	React with calcium ions to form CaCO ₃ , avoiding the formation of CaSO ₄ ; Requires heating; more efficient at high temperatures, from 323 to 353 K. (After this phase, the pH is 8.4)
Chemical pretreatment 3	NaOH and Na ₂ CO ₃	NaOH is added to neutralize the carbonic acid and remove the carbonate calcium hardness (same as 1); To increase the pH to a basic value (over 9) to favor the precipitation of Ca ²⁺ ; Na ₂ CO ₃ reacts with calcium to form CaCO ₃ , removing the temporary calcium hardness and avoiding the formation of CaSO ₄ . 0.4g/L NaOH; 2.5 g/L Na ₂ CO ₃ . (After this phase, the pH is 9.7)
Chemical pretreatment 4	/	Heat the solution during stirring to promote the precipitation of residual CaCO ₃ at high temperature
Chemical pretreatment 5	BaCl ₂	Produce insoluble barium sulfate (BaSO ₄); 9g/L BaCl ₂ in the brine; To prevent the calcium salt formation, the pH must be decreased to 5 using a buffer solution of hydrochloric acid (HCl).

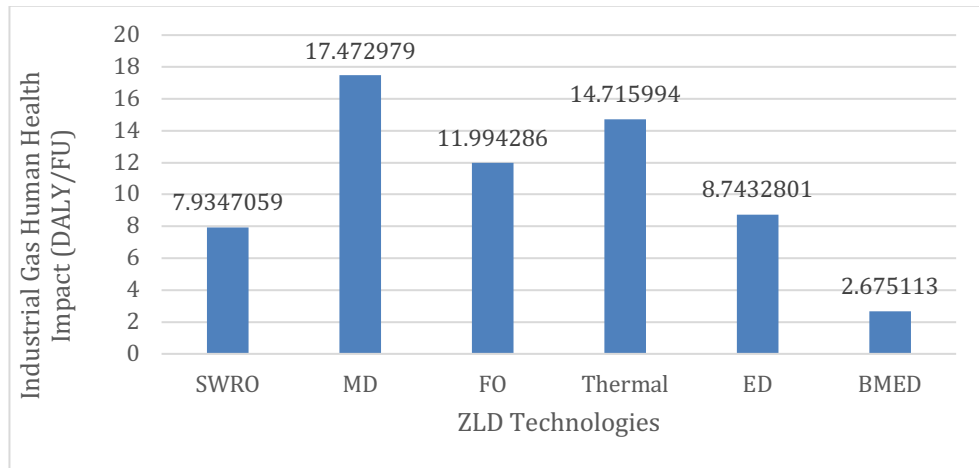
Chemical Use of MD Systems

Technologies	Source	CO2 emissions (kg/FU)	HUMAN HEALTH (DALY/FU)	Ecosystem (species.yr/FU)	Resource (USD2013/FU)
SWRO	COAL	479110.6	23.226402	0.020005932	10499.811
	GAS	103192.9	7.9347059	0.006351143	4672.1918
	NUCLEAR	1892.68	0.32862778	0.000297538	172.59683
	SOLAR	10608.05	3.364462	0.004673226	1047.1917
	WIND	2777.93	0.51421291	0.000439583	245.80283
	BIOMASS	123856.46	0.16706625	0.000506571	106.34725
MD	COAL	392483.9	27.485681	0.021094416	10792.158
	GAS	145534.1	17.472979	0.012153528	6976.3471
	NUCLEAR	79533.8	12.492669	0.008189747	4030.1007
	SOLAR	85274.2	14.480473	0.011054861	4602.7683
	WIND	80133.8	12.614186	0.008282755	4078.0346
	BIOMASS	159763.8	12.386881	0.008326617	3986.7218
FO	COAL	721148.237	35.043784	0.030177389	15786.314
	GAS	154271.691	11.994286	0.009595234	7002.2196
	NUCLEAR	1986.0605	0.52948209	0.000470507	219.88443
	SOLAR	15095.924	5.1054596	0.007066074	1538.18
	WIND	3323.943	0.80921851	0.000684615	330.2294
	BIOMASS	186480.0376	0.28595696	0.000785587	120.02504
Thermal	COAL	894156.248	43.323714	0.037307984	19530.397
	GAS	190308.812	14.715994	0.01176259	8628.0815
	NUCLEAR	1819.0284	0.48653499	0.000437501	210.23467
	SOLAR	18112.1	6.1659768	0.008623541	1846.4277
	WIND	3478.931	0.83372785	0.000703239	347.18854
	BIOMASS	231100	0.18428552	0.000828559	86.294898
ED	COAL	529113.32	25.633404	0.022077789	11579.183
	GAS	113204.65	8.7432801	0.006995676	5142.4085
	NUCLEAR	1808.89	0.34214514	0.000309294	172.4748
	SOLAR	11441.82	3.6953125	0.005142368	1138.4904
	WIND	2794.75	0.54712933	0.000466187	253.33297
	BIOMASS	860005.17	0.16369572	0.000540177	99.300217
BMED	COAL	160049.72	7.7679546	0.006693134	3526.9041
	GAS	34677.02	2.675113	0.002145458	1586.0376
	NUCLEAR	1077.18	0.14193741	0.000129328	87.464486
	SOLAR	3978.37	1.1530105	0.001586634	378.74502
	WIND	1368.9	0.20374584	0.000176636	111.84547
	BIOMASS	41815.17	0.088129958	0.000198946	65.400316

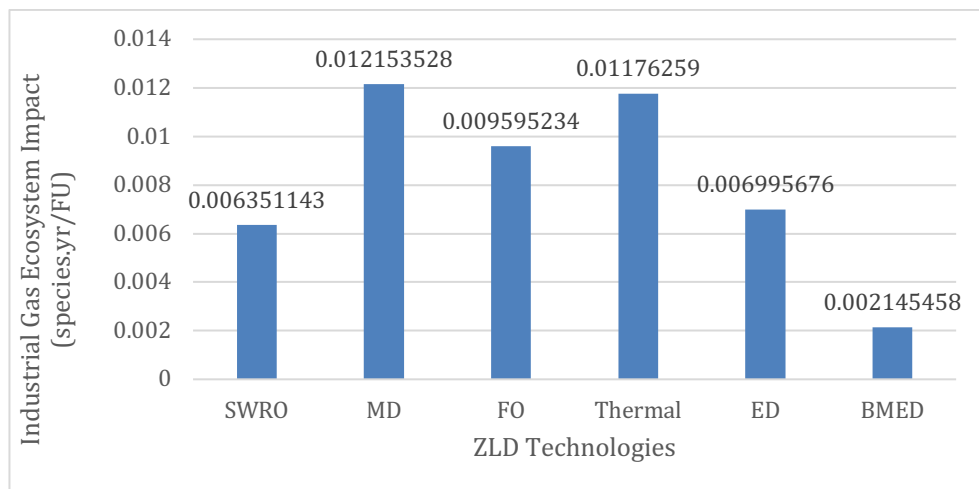
Impacts Assessments of 6 ZLD Technologies from 6 Different Energy Sources



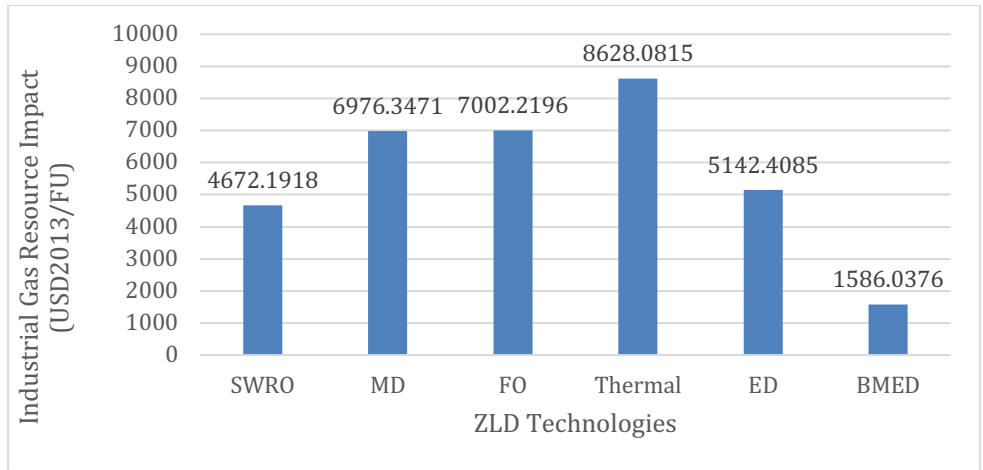
CO2 Emissions Using Industrial Gas Energy



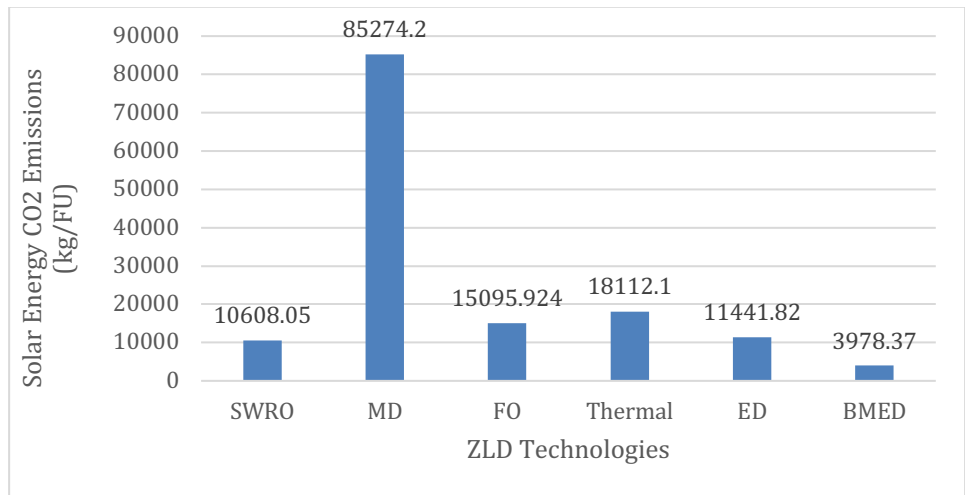
Human Health Impact Using Industrial Gas Energy



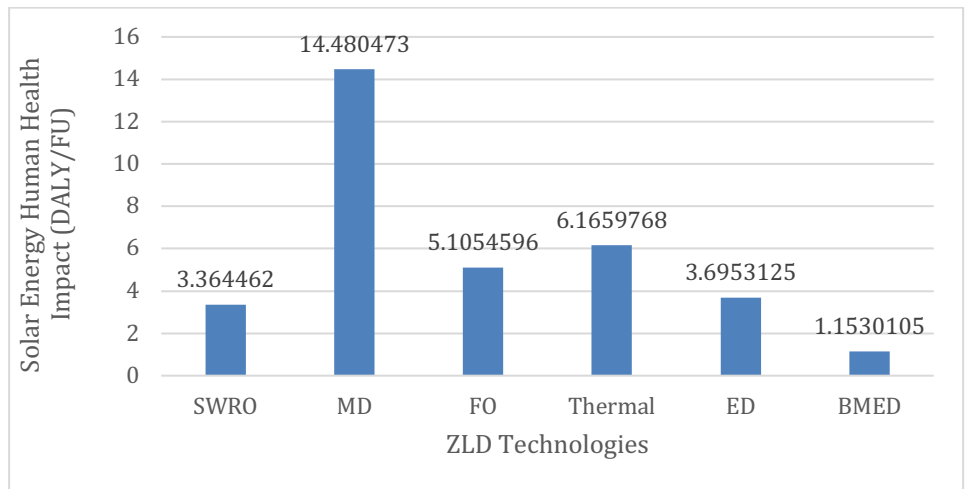
Ecosystem Impact Using Industrial Gas Energy



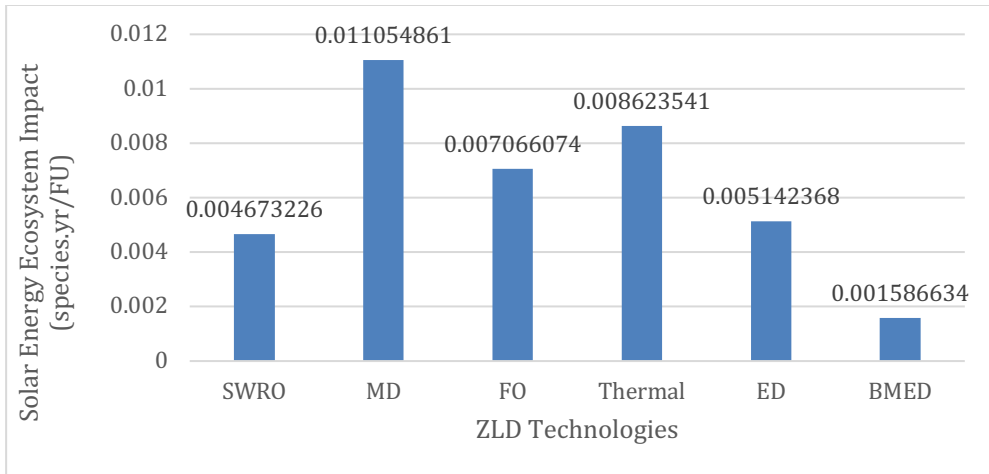
Resource Impact Using Industrial Gas Energy



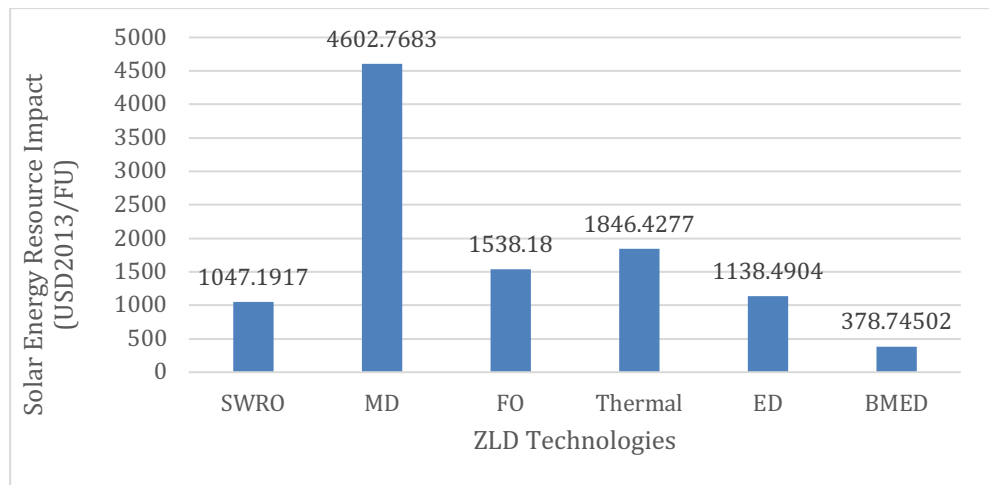
CO2 Emissions Using Solar Energy



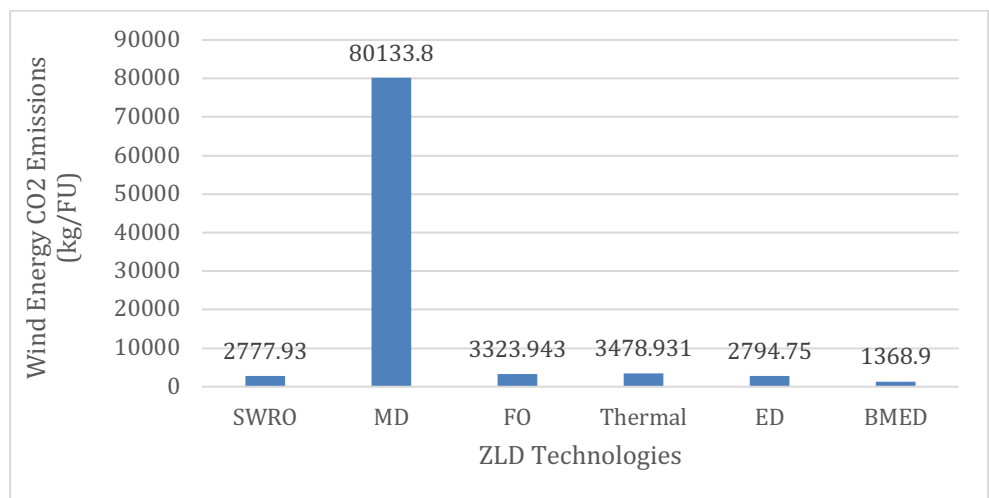
Human Health Impact Using Solar Energy



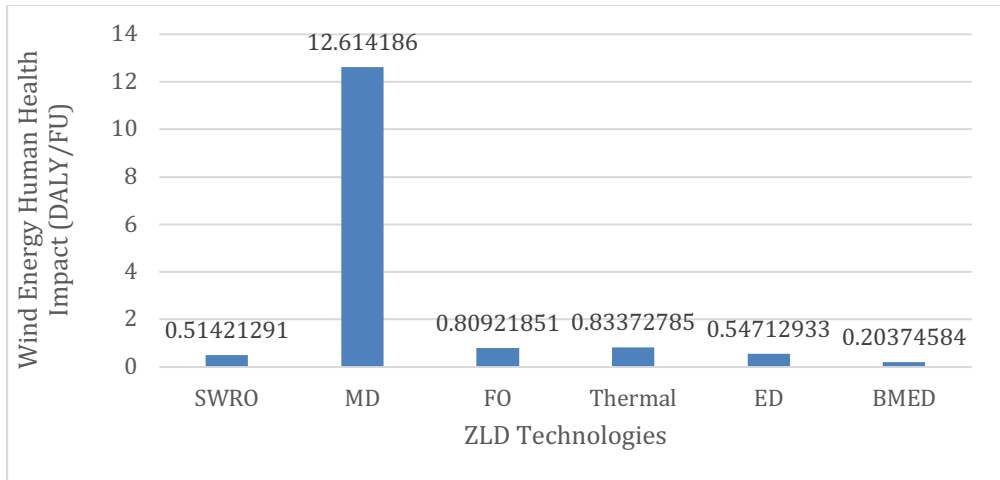
Ecosystem Impact Using Solar Energy



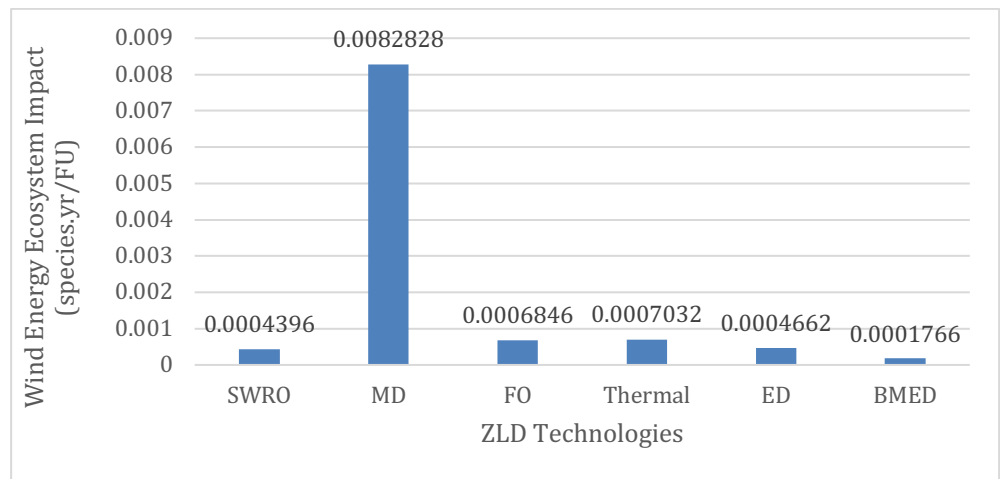
Resource Impact Using Solar Energy



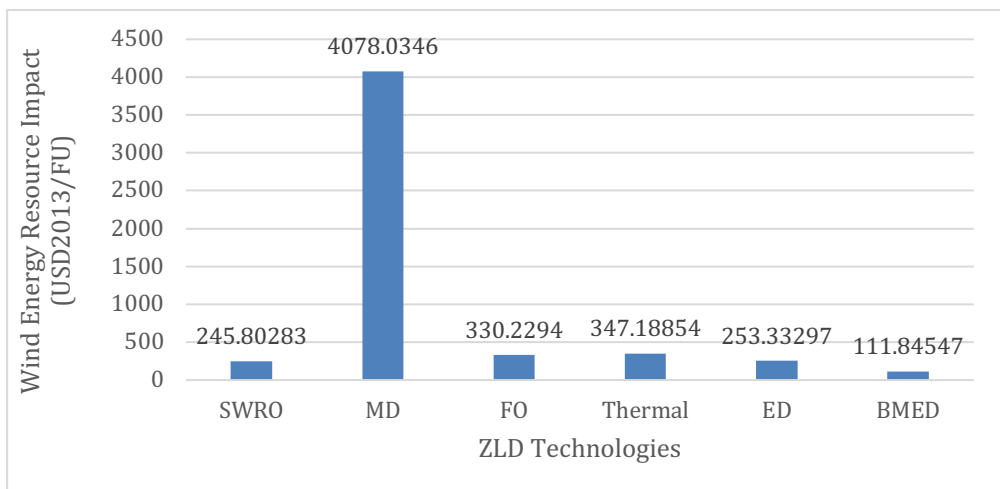
CO2 Emissions Using Wind Energy



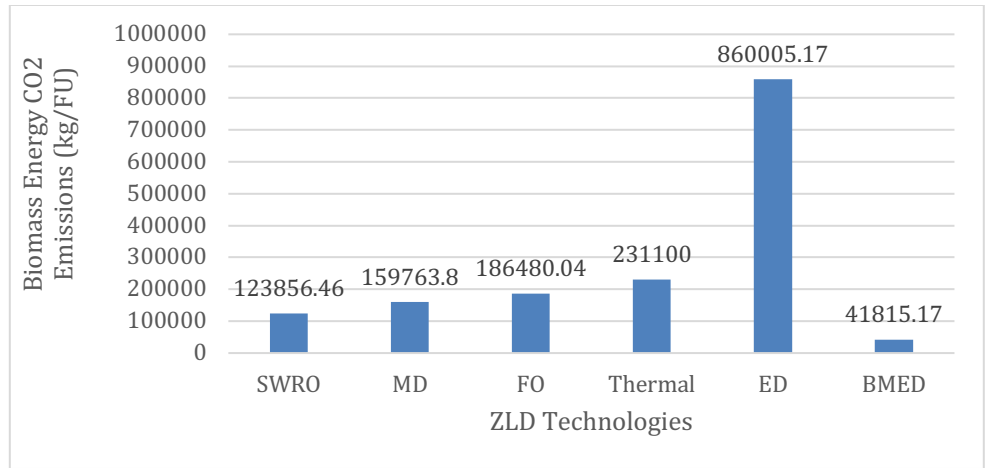
Human Health Impact Using Wind Energy



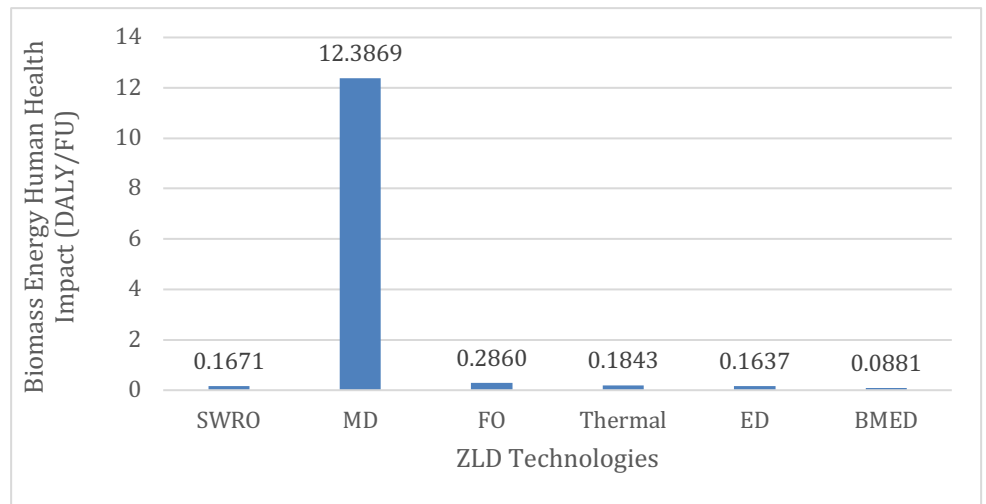
Ecosystem Impact Using Wind Energy



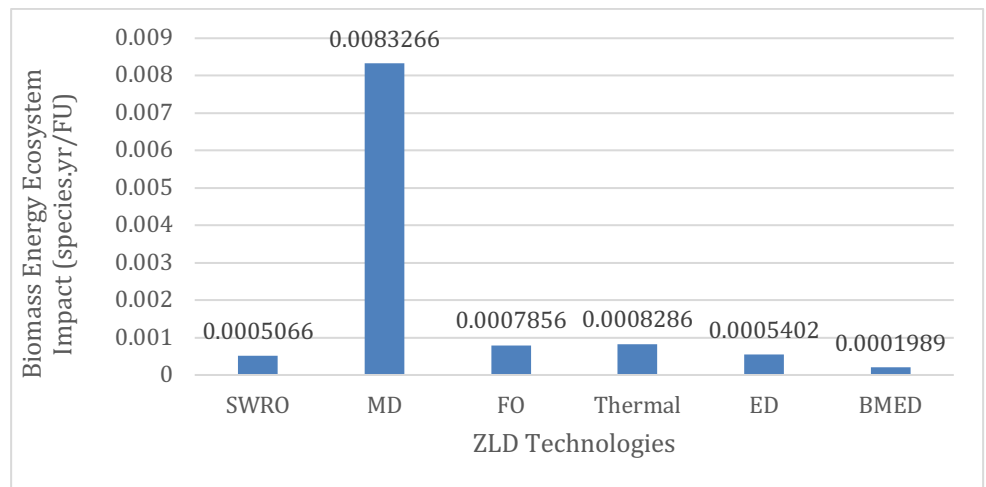
Resource Impact Using Wind Energy



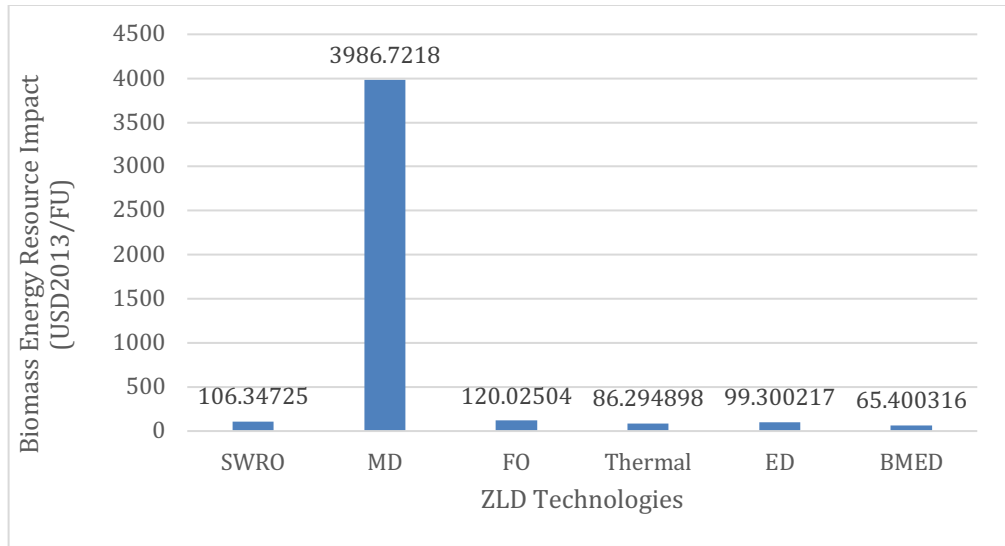
CO2 Emissions Using Biomass Energy



Human Health Impact Using Biomass Energy



Ecosystem Impact Using Biomass Energy



Resource Impact Using Biomass Energy

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