Summary

Water and energy are widely recognized as being interlinked and interdependent. On the one hand, water extraction, distribution and desalination require a great amount of energy. On the other hand, water is essential to carry out energy production in both the extraction industry and the field of renewables. The "water–energy" nexus is furtherly challenged by the increasing global population and its growing demands of freshwater.

An assessment of water reuse technologies applied to the energy sector is therefore of key importance to better managing the resources available. A case-by-case assessment of the best technological approach must be carried out in order to reuse wastewater produced when extracting and harvesting energy, while exploiting the best source of energy available to run the same water reuse scheme.

This thesis investigates and develops water reuse techniques in three relevant emerging applications related to energy production. The first two case studies are related to enhanced oil and gas extraction activities, which represent applications that currently able to meet the short-medium energy demand. Such activities, based on hydraulic fracturing and polymer flooding techniques, are raising particular concern due to their significantly high water demand and growing implementation. Among possible water treatment technologies, thermally driven processes are particularly adaptive for the recovery of hypersaline produced water. In fact, shale oil and gas reservoirs are usually characterized by abundant geothermal heat which can be exploited to drive thermal desalination processes. In particular, membrane

distillation is recently gaining considerable interest due to its compact and modular configuration. In membrane distillation, the saline feed water is heated before being contacted with the cool permeate stream across an air-filled hydrophobic membrane. Due to the low liquid affinity with the membrane surface, water vapor can be easily produced from the feed to the permeate side under relatively low temperature if compared to other evaporative technologies. In the first case study, membrane distillation technology is applied for the treatment of produced water deriving from hydraulic fracturing application. Here, the advanced oxidation pretreatment before membrane distillation allowed the removal of surfactants and to obtain an overall water recovery above 70%. The quality of the effluent deriving from the Fenton-membrane distillation coupled treatment was adapted for further in-situ reuse, diminishing the overall freshwater demand within the extraction process. Moreover, fouling was investigated under different operative conditions in membrane distillation. The accumulation and consequent flux decline was mainly dominated by the feed inlet temperature. The cross-flow velocity mainly influenced the final fouling thickness, which was monitored in-real time under continuous operation by non-invasive optical coherence tomography technique.

When the target is the treatment of produced water deriving from polymer flooding application, the presence of divalent ions in the stream can be exploited to induce the phase separation of the polymer under certain specific pH and temperature conditions. In this innovative treatment solution, the increment of the pH was revealed to be the most effective parameter to induce polymer precipitation.

Ultrafiltration membranes were also investigated for the treatment of polymer flooding produced waters. This technology resulted effective when 15 kDa cut-off membrane was used, which provided the best combination of productivity (100 LMH under 1 bar applied pressure) and polymer removal (92%). Overall, the best approach to obtain high-quality effluents from the treatment of produced water deriving from polymer flooding extraction would be to couple precipitation and ultrafiltration within the treatment train, as the two methods appear to complement each other in several ways.

The last case study aims to increase the competitiveness of renewables compared to non-renewable energy sources by promoting the sustainable harvesting of microalgae as a promising bioenergy alternative. Differently from other renewable sources, bioenergy can operate under continuous energy output without requiring energy storage. However, a large amount of freshwater is required for algae to grow, live, and reproduce. The volumes of water that need to be treated and moved, and the associated energy, still limit the competitiveness of this technology with non-renewables. From this perspective, in-situ water reuse applied to this technology would promote the importance and effectiveness of biofuel production. Among harvesting techniques, membrane filtration seems to be particularly adaptive as able to highly concentrate the micro-sized biomass without damaging cells and without using chemicals which might impair the water quality of the potentially reusable effluent. In the last case study, an innovative water reuse approach has been investigated for three different algae species such as Spirulina, Chlorella and

Scenedesmus by carefully evaluating the permeate quality obtained with four different membranes ranging within the micro to ultrafiltration range. TiO_2-based tubular ceramic membranes entirely made of high purity materials were used for the recovery tests, being particularly suitable for bio-technological applications and because of the possibility of sterilization by superheated water and oxidizing agents. As in the previous investigation, related to water reuse in polymer flooding applications, ceramic membranes were tested in both micro and ultrafiltration ranges. A wider range of nominal pore size was investigated in this case study to cover the whole size distribution of the different tested algae cells and their related algal organic matter. Specifically, ceramic membranes in the range between 0.8 μm and 15 kDa successfully concentrated biomass. Above 15 kDa, the stabilized productivity was in the range of 60-120 L $m^{-2}h^{-1}$, achieving a biomass concentration between 1.6 and 2 g/L at the end of three hour tests. Differently from polymer flooding applications, the 15 kDa pore size did not allow sufficient water flux. Within the selected pore size range, whole algae cells were rejected nearly at 100% rate. Instead, membranes retained between 40 and 90% of the small-size or dissolved organic molecules. Nutrient passage was almost complete (80 to 95%), allowing permeate reuse for further biomass growth. Satisfying growths of algae in the reused permeates were observed with the combinations: (i) *Scenedesmus o.*-0.14 μm membrane; (ii) *Chlorella s.*-300 kDa membrane. For those specific conditions, almost 50% of the water volume may be recovered and reused, drastically reducing the freshwater and nutrients demand of the cultivation process.

Overall, the results of this dissertation are aimed at promoting more sustainable processes to produce energy. The study investigates the site-specific factors that can be exploited to increase water recovery, while lowering the overall costs and the environmental impacts. This insight is expected to generate considerable interest in the exploration of novel systems, and therefore broaden the picture to more sustainable engineering applications.