

Treatment System of Produced Water with Supercritical Carbon Dioxide

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Abstract. Produced water from oil and gas exploration and production, contains naturally occurring dispersed and dissolved compounds, including aromatic hydrocarbons, organic acids, phenols as well as traces of chemicals added in the production/separation line. These hydrocarbons must be removed before water can be released to the environment. A suggested process, based on extraction to remove hydrocarbons from produced water using supercritical CO₂ as extracting agent. The process was simulated using Aspen HYSYS v7.3, utilizing Peng Robinson Property Package to calculate the system thermodynamic properties. The process was run at the optimum conditions, which were found by running an optimization routine on the main factors affecting the process. The conditions are 32°C, 91 bar, and 1:1 mole of scCO₂ to water results from the simulation process showed that scCO₂ was very effective in removing all the hydrocarbons from produced water, and recovery of 99% of the treated water.

Keywords: Supercritical CO₂, Produced Water, Extraction, Aspen Hysys.

1. Introduction

Produced water is a by-product of the production of oil and gas from underground reservoirs. It accounts for a significant waste stream in the countries producers of oil and gas. Produced water production estimates are in the order of 250 million B/D in 2007, for a water-to-oil ratio around 3:1, and are expected to increase to more than 300 million B/D between 2010 and 2014 [1]. This is by some estimates the largest single waste stream in the US [2]. Whereas re-injection (for enhanced recovery or disposal) accounts for as much as 95% of this water [3], the remaining fraction is still considerable. Re-injection is not always feasible because of geographic and cost considerations. In the case of offshore waters (Gulf of Mexico), for instance, discharge is the most practical and cost effective means of handling the waste stream. Some on-shore waters of lower salinity, for example, in areas of east Texas, are exempt from required re-injection and are frequently used for beneficial uses such as stock or crop watering [4]. In these situations, however, it may be desirable, and often necessary from a regulatory viewpoint, to treat produced water before discharge. It also may be feasible to treat waters that slightly exceed regulatory limits for reuse in arid or drought-prone areas, rather than losing them to re-injection. Also, increasingly stringent environmental regulations require extensive treatment of produced water before discharge; hence the treatment and disposal of such volumes cost the industry annually more than USD 40 billion. Consequently, for oil and gas production wells located in water-scarce regions, limited freshwater resources in conjunction with the high treatment cost for produced water discharge makes beneficial reuse of produced water an attractive opportunity [5].

The chemical composition of produced water has been described by several authors [6]-[8]. Results of analysis of aromatic compounds are being developed and they were one of the main topics discussed at a

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workshop held in Voorburg in October 2001[9]. Produced water contains naturally occurring dispersed and dissolved compounds, including aromatic hydrocarbons, organic acids, phenols as well as traces of chemicals added in the production/separation line. Its chemical composition varies over a wide range and depends mainly on attributes of the reservoir's geology. The composition of produced water may also change slightly throughout the production lifetime of the reservoir [10].

Supercritical Carbon dioxide (scCO₂) is the best supercritical fluid in the field of extraction of heat-sensitive components due to its chemical and physical properties and its low critical temperature and pressure[11]. The main purpose of this study is to develop a process to extract hydrocarbons from produced water by supercritical carbon dioxide before the usage of this water or discharge it to the environment.

2. Materials & Methods

2.1. Composition of Produced Water

The main hydrocarbon compounds in produced water are aliphatic and aromatic. Aliphatic compounds include alkanes, alcohols and carboxylic acids; and aromatic compounds include BTEX, PAH, NPD and phenols. Table 1 shows detailed hydrocarbons' analysis of produced water from one of the production fields operating in Libya. The well produces 10,000 m³/day (≈ 64,000 bbd) produced water. The data collected from one oil well, and represent the average of three samples.

Table 1: Concentration of hydrocarbon compounds in produced water

<i>Compound</i>	<i>Quantity</i>	<i>Concentrations</i>
	<i>Kg/hr</i>	<i>mg/l</i>
<i>Water</i>	42000	--
<i>Benzene</i>	6.2874	149.0258
<i>Phenol</i>	0.6468	15.33065
<i>Toluene</i>	2.4612	58.3361
<i>Ethyl benzene</i>	0.2373	5.624556
<i>m-Xylene</i>	0.5460	12.94146
<i>p-Xylene</i>	0.4469	10.59256
<i>o-Xylene</i>	0.1390	3.29462
<i>m-Cresol</i>	0.1050	2.488741
<i>Naphthalene</i>	0.3530	8.366912
<i>2,7-Dimethylnaphthalene</i>	1.2180	28.8694
<i>2,6-Diethylnaphthalene</i>	1.3482	31.95544
<i>Propylene-naphthalene</i>	0.8744	20.72529
<i>Phenanathrene</i>	0.4502	10.67078
<i>Dibenzothiophene</i>	0.1407	3.334913
<i>Chlorobenzene</i>	0.0080	0.189618
<i>p-Cresol</i>	0.1344	3.185589
<i>Anthracene</i>	0.0011	0.026073
<i>Fluoranthene</i>	0.0015	0.035553
<i>Pyrene</i>	0.0032	0.075847
<i>Chrysene</i>	0.0064	0.151695
<i>Fluorene</i>	0.0280	0.663664
<i>Acebaphthalene</i>	0.0026	0.061626
<i>Acenaphthalene</i>	0.0064	0.151695
<i>DinC4 phtahalte</i>	0.0067	0.158805
<i>n-C17</i>	41.1600	975.5866
<i>n-C18</i>	27.7000	656.5537

2.2. Supercritical Carbon Dioxide (scCO₂)

Supercritical fluid is a substance above its critical temperature and pressure. Under these conditions the distinction between gases and liquids does not apply and the substance can only be described as a fluid. Carbon dioxide above its critical temperature T_c (31°C) and critical pressure P_c (73.4 bar) behaves as a supercritical fluid, expanding to fill its container like a gas but with a liquid density.

Supercritical carbon dioxide (scCO₂) is an excellent non-polar solvent for many organic compounds. It has been linked to a solvent resembling hexane, though with some hydrogen-bonding acceptor capability and

some dipole selectivity. In which, alkenes, alkanes, aromatics, ketones and alcohols (up to a relative molecular mass of around 400) dissolve in scCO₂. Very polar molecules such as sugars or amino acids and most inorganic salts are insoluble. By adjusting the pressure of the fluid, the solvent properties can be adjusted to be more 'gas-like' or more 'liquid-like', which allows 'tuning' of the solvent properties. Supercritical CO₂ is an important commercial and industrial solvent due to its role in chemical extraction in addition to its low toxicity and environmental impact. The relatively low temperature of the process and the stability of CO₂ also allow most compounds to be extracted with a little damage or denaturing[12].

2.3. Modeling and Description of Simulated Process

Modeling is carried out using HYSYS v7.2, and the process flow diagram (PFD) is shown in figure 1. The extraction column was run with stage efficiency of 0.25, and an optimization routine was run over the process main factors, temperature, pressure, and scCO₂ flow rate. Wastewater enters the extraction column (T-100) using pump at the column conditions (32°C and 91bar). The extraction column is a unit where wastewater flows down and scCO₂ liquid flows up. Both phases come to contact by the help of column plates or random or structured packing. Hydrocarbons are transferred from the wastewater to the scCO₂ where they bind with it depending on their polarity. Essentially all the hydrocarbons are removed from the water. The treated water in Stream 13 contains some dissolved CO₂, is throttled and flashed in three separators respectively (V-100, V101 and V-105) to gas the CO₂ and collect it in (MIX-103) then sent to a final separator stage (V-106) to remove a content of condensate water in CO₂, then recycled in stream 25. The treated water is then cooled at atmospheric pressure. The process yield of treated water is about 99%.

scCO₂, some water, and the entire hydrocarbons exit the top of the extractor (Stream 12) are throttled and heated to change the scCO₂ to the gas phase and separate it from water and hydrocarbons in (V-102). The CO₂ is compressed in K-102 and cooled in E-107 to (40 bar and 4.85 °C) then flashed in (V-103) to separate the remaining hydrocarbons that interacting with CO₂, that exit from the bottom of (V-103) which throttled to atmospheric pressure and flashed in (V-104) to vaporize and send the hydrocarbons to (MIX-100) where they are flared to produce a pure CO₂ that can be used as a make-up CO₂ to the process or liquefied and stored in cylinders.

In (V-103, V-104 and V-106), the CO₂ exit the top of the column is recycled in stream 36. The residual CO₂ in stream 37 is combined with the CO₂ in makeup stream. The CO₂ in stream 38 is then compressed and cooled to the operating conditions and recycled to the extractor. Essentially about 80% mol. of the CO₂ is recovered and recycled. However, if any make-up CO₂ is needed, it can be added to the CO₂ stream entering the extractor.

3. Results & Discussion

The simulation process showed that csCO₂ is very effective in removing hydrocarbons from produced water. The yield of the treated water was about 99% and free of hydrocarbons, though contained small amount of dissolved CO₂ (about 1.9 ppm), which far below the allowed concentration of CO₂ in drinking water according to Libyan standard (24-30 ppm). The recycled scCO₂ represents 80% of its original amount. The removed hydrocarbons from produced water were sent to flare (streams 27 and 37), and the produced CO₂ was directed to makeup for lost CO₂.

The main factors affect the extraction processes are temperature, pressure, and csCO₂ flow rate. An optimization routine was run on these factors, and found the optimum conditions are 32°C, 91 bar, and 1:1 mole of scCO₂ to water. One factor at a time approach was used to study the effect of each factor on the process. The goal of the process was to get the highest yield, separation at the lowest cost.

In the case of temperature, the amount of recovered water decreased with increasing temperature in the range of 32 to 40°C. The change is not significant, when the temperature decreased to below 32°C, the separation falls significantly, and that is probably because of the closeness to the critical temperature. At temperature lower than the critical temperature, the interaction rate will be too slow and the separation decreases. Above 40°C, the process diverged, and the number of stages should be increased. However, when the column diverges and the number of stages, the % hydrocarbons removal and heat consumption is close to a maximum. Increasing the number of stages will increase the cost, therefore it is recommended to keep the

temperature at 32°C below 40 °C and little higher T_c . The optimum temperature is a trade-off between improved hydrocarbons removal and gasification of the $scCO_2$.

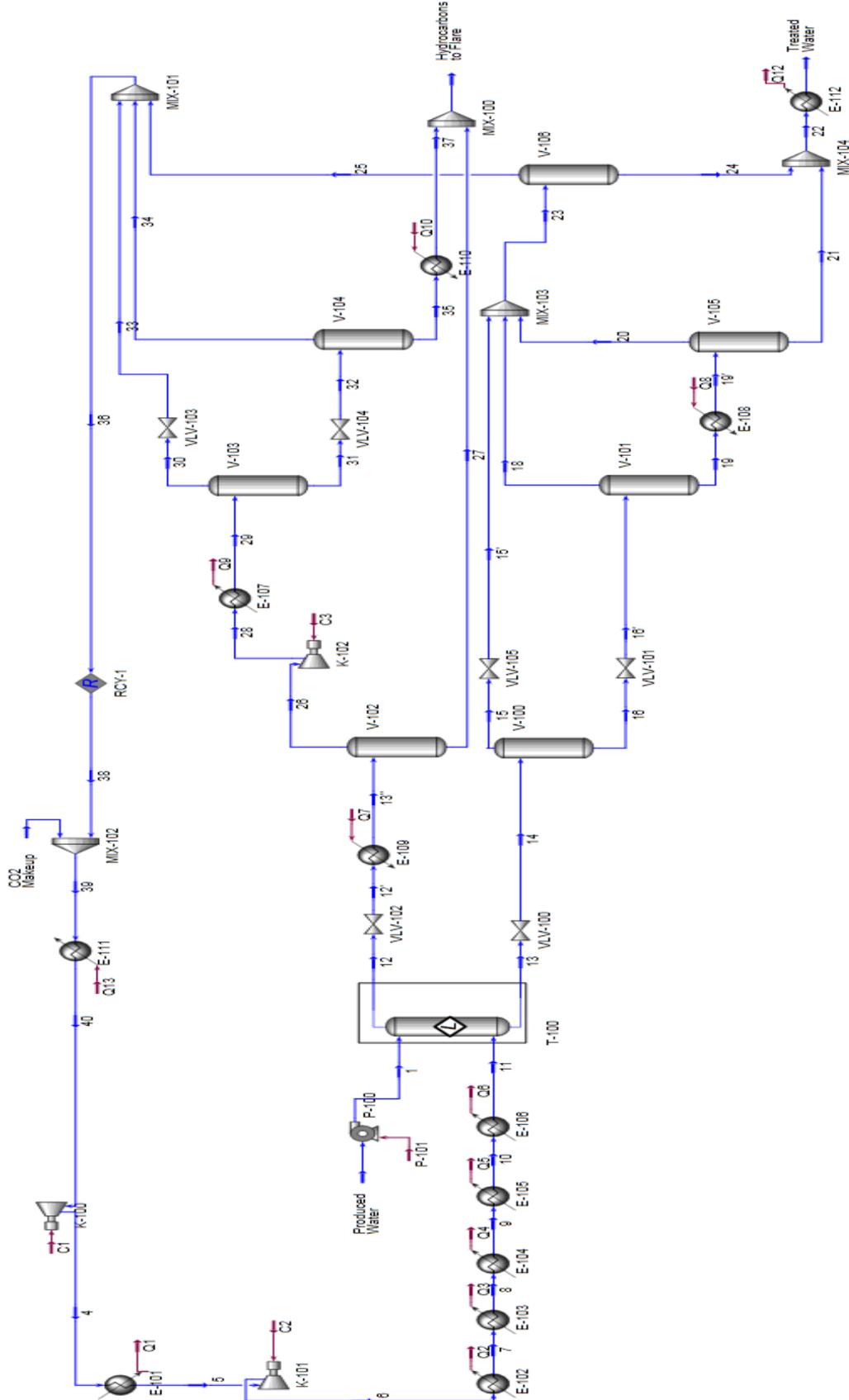


Fig. 1: PFD for produced water treatment process by extraction by $scCO_2$.

The optimum pressure range was from 87 to 141 bar. The change in the optimum range is not significant; therefore it is less expensive to choose the lower pressure, which is 87 bar. Below 87 bar and above 141 bar,

the process diverges and the number of stages needs to be increased. It is not obvious whether the convergence difficulties are due to physical limitations, or if it is a numerical problem. There is a trade-off between hydrocarbons removal efficiency and cost of column and pressure drop. The pressure must be consistent with the pressure of the scCO₂ solution leaving the extractor. The problems of limited range of temperatures and pressures are probably related.

At these optimum process conditions (87 bar and 32°C), the optimum scCO₂ flow rate is found to be 1:1 mole ratio to waste water flow rate enters the column. A less ratio than the optimum will result in less hydrocarbons' separation; and higher ratio than the optimum will flood the column by scCO₂. The recycled scCO₂ represents 80% of the original amount entered the extractor unit. The developed model can be further improved by the integration of heat streams of the process, which should result in overall energy optimization and total cost reduction.

4. Conclusion

An extraction process for hydrocarbons removal from produced water using scCO₂ as extraction solvent was developed using Aspen HYSYS model. The process succeeded in removing all hydrocarbons from produced water, and in recovering more than 99% of treated water and 80% of used scCO₂. The extraction unit stages were kept low, and the operating conditions of the process were optimized and kept close to critical conditions. The model is flexible and improvable, and most importantly is practicable. Experimental studies will be carried out to develop this process and present it as a new resource for usable water and environmental protector.

5. References

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