Treatment System of Produced Water for Oil and Gas Industry

Hesham G. Ibrahim[1] and Aly Y. Okasha[2]

[1]*Chemical Engineering Department, Faculty of Engineering, Misurata University,*
Al-Khoms City, Libya.
Tel.: ++218-338-9965, e-mail: h_g_ibrahim@yahoo.com

[2]*Environmental Department, Faculty of Science, Misurata University, Al-Khoms City, Libya*
Tel.:++218-91-344-6102, e-mail: aly_okasha2002@yahoo.com

Abstract

Produced water is a by-product of the process of oil and gas production from underground reservoirs. This co-produced water from the oil and gas industry accounts for a significant waste stream in the countries producers of oil and gas. 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. These hydrocarbons must be removed before water can be released to the environment. One method for removal of hydrocarbons from wastewater is extraction. So, a suggested process based on extraction process to removal hydrocarbons from produced water using CO_2 at supercritical case as extracting agent. Removal process has been simulated with the process simulation tool (Aspen HYSYS). Peng Robinson and hydrocarbons Property Package models were used to calculate the system thermodynamic properties. The simulation process was very effective in removing all the hydrocarbons from produced water and 99% of the treated water was recovered. Also found this method to be economically competitive with the alternatives (include incineration, wet air oxidation, and biological processes).

1. INTRODUCTION

Produced water is a by-product of the production of oil and gas hydrocarbons from underground reservoirs. Co-produced water from the oil and gas industry accounts for a significant waste stream in the countries producers of oil and gas. For each barrel (bbl) of oil produced, an average of 10 bbl of water is produced for an annual total of about 3 billion tons (API, 1987). This is by some estimates the largest single waste stream in the US (Allen and Rosselot, 1994). Whereas re-injection (for enhanced recovery or disposal) accounts for as much as 95% of this water (IOGCC, 1993), 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, (Sullivan et al., 2004). 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.

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 dependents mainly on attributes of the reservoir's geology. The composition of produced water may also change slightly through the production lifetime of the reservoir (OGP, 2003).

Oil and gas reservoirs contain a mixture of oil, gas and water at equilibrium, a small proportion of the hydrocarbons will be dissolved in water as a result of their inherent solubility. Different hydrocarbons compounds have different solubility's in water and aromatics hydrocarbons are relatively more soluble than aliphatic hydrocarbons. There will, therefore, be a small dissolved hydrocarbon component in the produced water consisting of light aromatic hydrocarbons, in addition to suspended oil droplets.
The treatment processes for separation of oil and water before discharge of the produced water have until now been based on the use of gravitational force, utilizing the difference in specific gravity between oil droplets and water. The oil droplets will generally float to the top of the water phase where they can be removed. Gravity treatment methods are not able to remove dissolved hydrocarbon components.

Aromatic compounds have one or more ring structures and are held together in part by particularly stable bonds that contain delocalized clouds of so-called π-electrons. Benzene is the simplest of this class of compounds, consisting of 6 carbon and 6 hydrogen atoms (monoaromatic compound). Polycyclic Aromatic Hydrocarbon compounds (PAH, occasionally also termed Polynuclear Aromatic Hydrocarbons) refers to hydrocarbons containing two or more fused benzene rings. Due to the wide range of concentrations of these compounds in produced water from different oil and gas fields, and also difference in potential for causing environmental effects, the compounds are divided into three groups;

- BTEX: Benzene, toluene, ethylbenzene, and xylene (ortho, meta, and para isomers) these are monocyclic aromatic compounds.

- *NPD*: naphthalene and phenanthrene and dibenzothiophene, including their C1-C3 alkyl homologous. These are 2-3 ring aromatic compounds.

- *PAH*: Polycyclic aromatic compounds, represented by the 16 EPA PAH (except naphthalene and phenantherene, which are included in the NPD group). These are 3-6 ring aromatic compounds.

The chemical composition of produced water has been described by several authors (Brendehaug et al., 1992; Sørstrøm, 1993; Utvik, 1999). Many of the studies listed, however results of analysis of aromatics compounds are being developed and they were one of the main topics discussed at a workshop held in Voorburg in October 2001(IAOGP, 2002).

Table 1: Concentration range (mgl^{-1}) of aromatic compounds in PW from oil fields in the North sea (1999-2001) (IAOGP, 2002)

Sector	*N*	*UK*	*NL*	*DK*
Production	*Oil*			
BTEX	0.7-24.1	1.9-36	0.042-4.8	8.7-14
NPD	0.8-10.4	0.24-0.8	N/A	0.22-0.436
PAH	0.001-0.13	0.003-0.05	0.0026-0.1545	0.12-0.285

Studies of chemical composition of aromatics compounds from on specific field over a period of one week show that there is little variation in composition during that time span (Utvik, 1999). Results from annual environmental reports and data from the Norwegian Oil industry Association (OLF) produced water data base show that the composition of produced water is also relatively constant from one year to another at individual fields.

Imparts of produced water constituents in altering habitat integrity of the natural bodies have been reported in previous studies (Ajayi and Osibanjo, 1981). It explains that, if untreated produced water is discharge or allowed to accumulate, the decomposition of organic materials it contains can lead to production of large quantities of malodorous gases. All these causes damage to human health, fisheries, and agriculture and results in associated health and economic costs (Okpokwasili and Nwabuzor, 1988). For these reasons, the immediate treatment and disposal, is not only desirable but also necessary in an industrialized society. This is mandatory by numerous federal and state laws. The ultimate goal of produced water management is the protection of the environment in a manner commensurate with public health, economic, social and political concerns.

In the case of lower-salinity water, the removal of organic compounds becomes more important to meet requirements or esthetic considerations for beneficial reuse. Low-cost, simple technologies are desirable so that small producers or isolated production areas can use the process easily. Sorption of organics by surfactant-modified zeolite (SMZ) followed by air stripping and subsequent treatment of the off-gas by a vapor-phase bioreactor (VPB) has been shown to be effective at removing BTEX from produced water and is a simple, cheap process that is cost-competitive with other sorption-based technologies (Katz, et al., 2003, Sullivan,et al., 2004). Costs evaluated included membrane filtration, carbon adsorption, chemical oxidation (hydrogen peroxide and ozone), air stripping, UV oxidation, and reinjection. Costs for these treatment processes ranged from \$ 0.20 to \$ 8.33 per 1000 gallons of water. But as a matter of facts the main problems is needed to regenerations has a main disadvantage, in which the studies by (Sullivan et al., 2004) don't gave a solution to removal other hydrocarbons in produced water such as other aromatics (NPD and PAH). So, the main concern of this work is developing a process to remove of hydrocarbons from produced water by extraction process using supercritical CO2; before this water can be released to the environment. Carbon dioxide (CO2) 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 values, (Goto et al., 2008). From literature found this method to be economically competitive with the alternatives. These alternatives include incineration, wet air oxidation (supercritical water oxidation), and biological processes.

2. USED AVAILABLE MATERIALS

2.1 Composition of Produced Water

The main hydrocarbons compounds in produced water are clarified as following;

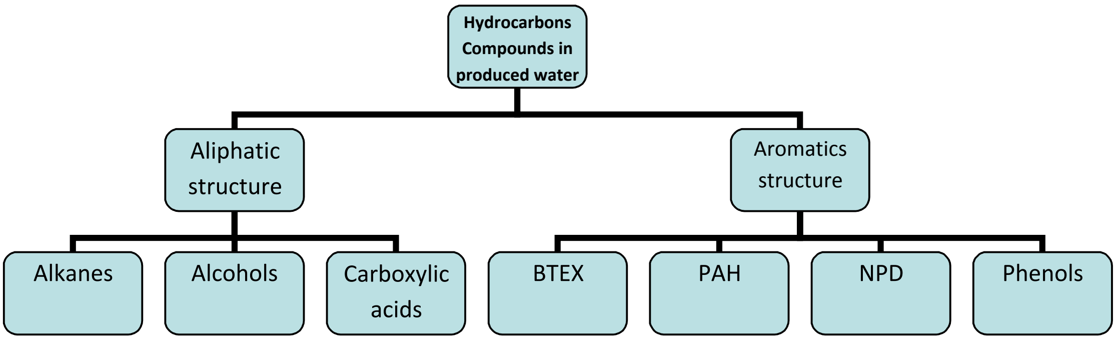

Figure 1: Classification of hydrocarbons compounds presents in produced water

Results from detailed characterization with regard to hydrocarbons for each one of national production fields operated in Libya (capacity of produced water is 10,000 m^3/day [≈ 64,000 bbld]). The data shown in Table (1) are average concentration based on analysis of three replicate samples for line capacity 1010 m^3/day.

Table 2: Concentration of hydrocarbon compounds in produced water

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

The most abundant aromatic compounds in produces water, the BTEX compounds are volatile and will evaporate rapidly from produced water discharge close to the sea surface or from produced water discharge plumes reaching the surface due to density gradients, (Terrends and Tait, 1996).

The NPD compounds are less volatile, but will also evaporate to some degree. This is particularly important for high temperature produced water discharges, or for produced water with a gas/air injection before discharge.

The less water-soluble fraction of aromatic compounds, the PAH compounds is expected to be associated with particulates and oil droplets in the produced water. As the discharge plume for most fields will rise towards the surface after discharge (principally due to its temperature), these compounds will follow the plume, or be retained at certain depths of the water column depending upon the bouncy of the supporting particulate matter.

Aromatic hydrocarbons span the whole range from readily to poorly biodegradable, depending on the nature of the actual compound. Biodegradation half-lives ranging from less than a day up to several months are described in the literature (Johnsen et al., 2000), with the lower molecular weight (and more abundant) compounds being more degradable.

2.2 Supercritical Carbon Dioxide (scCO2)

A supercritical fluid is a substance above its critical temperature and critical pressure. Under these conditions the distinction between gases and liquids does not apply and the substance can only be described as a fluid.

Left side of Figure (2) shows a substance in a sealed glass vial below its critical temperature and pressure existing as a liquid with vapor above it. As the temperature is raised, the liquid density falls due to expansion and the gas density rises as more of the substance evaporates. The densities approach each other and the meniscus between the two phases becomes less distinct, as shown in the middle of Figure (2). Eventually, at the critical point, the densities become identical, as shown on the right. Other properties also become identical and the distinction between liquid and gas disappears.

Above 304 K (31 ^{o}C) and 73 atm carbon dioxide behaves as a supercritical fluid and shows properties of both a liquid and a gas. It fills the container, like a gas, and dissolves substances like a liquid. A pressure-temperature (P-T) phase diagram, shown in Figure (2), illustrates the nature of a supercritical fluid. The range of pressures and temperatures that define the supercritical fluid region of the diagram are shown in the figure. Supercritical fluids are able to spread out along a surface more easily than a true liquid because they have lower surface tensions than liquids. At the same time, a supercritical fluid maintains a liquid's ability to dissolve substances that are soluble in the compound, which a gas cannot do (PNPPRC, 1999). In the case of scCO2, this means oils and other organic contaminants can be removed from a surface even if it has an intricate geometry or includes cracks and crevices.

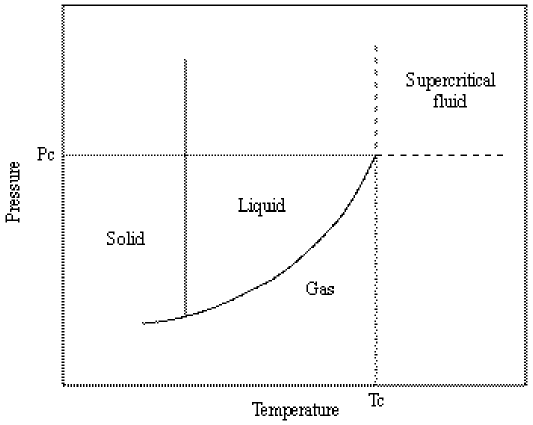

Figure 2: Phase diagram of CO2, (PNPPRC, 1999)

Supercritical carbon dioxide (scCO2) is an excellent non-polar solvent for many organic compounds. It has been likened 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 . The main advantages to use a scCO2 as a solvent are shown in Table (3);

Table 3: Advantages and disadvantages of scCO2 uses as a solvent

Advantages	*Disadvantages*
Non-toxic	Needs high pressures
Non-flammable	Greenhouse gas
Relatively unreactive	
Inexpensive	
Less solvent residues in products	
Lower environmental impact	
Has penetrating power of a gas, solvent power of a liquid	
Can be recycled	
Smaller solvent disposal costs	

3. AVAILABLE MODELS

3.1 Column models in simulation process

A hydrocarbons extraction column is a unit where wastewater flows down and scCO2 liquid flows up. Hydrocarbons is transferred from the wastewater phase to the scCO2 liquid phase where it binding with it depending on the polarity of these hydrocarbons. Both phases are made to get in contact by the help of column plates or random or structured packing.

3.2 Flow sheet convergence

All process simulation programs are based on modules for calculating different unit operations like heat exchangers, pumps, distillation columns..etc. Process simulation programs are traditionally divided into either sequential modular or equation based programs. In a sequential modular program, the in-streams of each calculation module must be known prior to the calculation, and the out-streams are the result of the module calculation. The programs Aspen Plus and ProVision are sequential modular. Equation based simulation programs can be able to calculate in-streams based on out-streams. Aspen HYSYS is an equation based simulation program.

However, also in Aspen HYSYS, the column models are based on specified in-streams. Because of this, flow sheets with columns in practice have to be calculated in a modular sequential manner.

4. DESCRIPTION OF SIMULATED PROCESS

The process flow diagram (PFD) is shown in Figure (3). Wastewater inlet to the extraction column (T-100) using pump at (30 ^{o}C and 111 atm). The extractor (T-100) is run counter currently and operating at (111 atm and 30 ^{o}C). Essentially all the hydrocarbons are removed from the water. In Stream 13, the treated water contains some residual CO2 and is throttled and flashed in three separators respectively (V-100, V101 and V-105) to degas of the water. The CO2 collected from these three stages are mixing in (MIX-103) then send to a final separator stage (V-106) to remove a content of condensate water in CO2 gas stream, then recycled in Stream 25. The treated water is then cooled to atmospheric pressure.

scCO2, some water, and all of the hydrocarbons exit the top of the extractor (Stream 12) and are throttled and heated to allow the scCO2 to become a gas and separate from the water and hydrocarbons in (V-102). The CO2 is compressed then cooled in K-102 and E-107 to (4000 kPa and 4.85 ^{c}C) then flashed in (V-103) to separate the remaining hydrocarbons that interacting with CO2, in which outlet from the bottom of (V-103) which throttled to atmospheric pressure and flashed in (V-104) to degas of the hydrocarbons that send to (MIX-100) then sending to Flare unit to producing a pure CO2 that can be used as a make-up CO2 to the process or liquefied and occupied in cylinders.

In (V-103, V-104 and V-106), the CO2 are taken off of 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 for recycle into 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. The yield of process of treated water is about 99% wt.

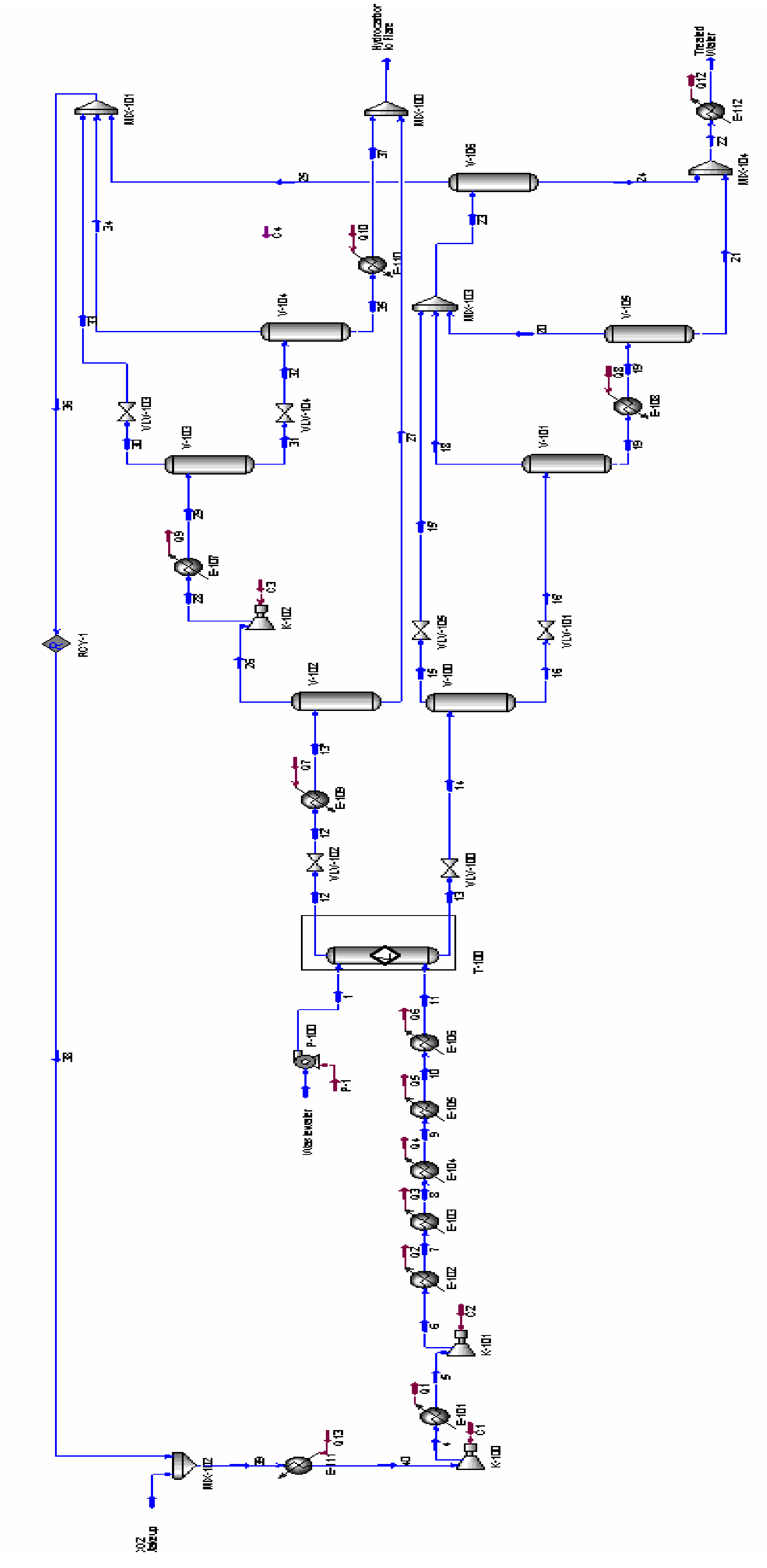

Figure (3) : PFD of produced water treatment by extraction with scCO2

5. RESULTS AND DISCUSSIONS

The simulation process was effective for hydrocarbons removal in which amount of treated water of the process was high and free of hydrocarbons and containing small amount of dissolved CO2 (about 1.9 ppm), anyway allowed concentration of CO2 in drinking water according to standard Libyan (24-30 ppm). Also, yield of the process of treated water is about 99% wt. All hydrocarbons removed from the produce water are concentrate and outlet in Streams (27+37) and go to flare to producing a pure CO2 that can be recycled again as a makeup CO2 to the process at feed point.

Different parameters have been varied to calculate the effects and to make a tool for optimizing the process. The only parameter that has a main effects found are the scCO2 flow rate and operating conditions. When the number of stages is increased, the performance of the process increases, but the calculation tends to diverge. However, when the column diverges due to too many stages, the % hydrocarbons removal and heat consumption is probably close to a maximum. A reduction in extraction temperature leads to improved performance. According to literature, a temperature of less than about 40 ºC is recommended.

All runs sets of supercritical conditions that were attempted (111 atm, 30.0°C; 155 atm, 30.0°C; 204 atm, 30.0°C). There was a noticeable difference, however, in the amount of time required to manipulation by HYSYS. At lower temperature, the interaction rates will be too slow. The calculations have been performed with constant column stage efficiencies of 0.25. The original Aspen HYSYS calculates efficiencies are temperature dependent. Temperature dependent stage efficiency is probably necessary to find an optimum extraction temperature.

It is not difficult to calculate the effects of extraction pressure drop. There is a trade-off between hydrocarbons removal efficiency and cost of column height and pressure drop. The optimum temperature is a trade-off between improved hydrocarbons removal and gasification of the scCO2. It is not obvious whether the convergence difficulties are due to physical limitations, or if it is a numerical problem. 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.

6. CONCLUSION

The hydrocarbons removal model developed by Aspen HYSYS is useful for evaluating the effects of using scCO2 as extraction solvent. The total efficiency in a process based on treated water product from system are excellent. The developed models can be developed further to improve scCO2 extraction process for hydrocarbons removal by changing operating conditions. The combination of heat streams for a process can be useful for heat integrated for total energy optimization and total cost optimization.

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Nomenclature of process

E-101 Wastewater cooler
E-102 Wastewater cooler
E-103 Wastewater cooler
E-104 Wastewater cooler
E-105 Wastewater cooler
E-106 Wastewater cooler
E-107 CO2 recycle cooler
E-108 Treated water heater
E-109 Extract heater
E-110 Hydrocarbons heater
E-111 CO2 recycle heater
E-112 Treated water cooler
K-100 1st Feed CO2 compressor
K-101 2nd Feed CO2 compressor
K-102 CO2 recycle compressor
MIX-100 Mixing point of outlet hydrocarbons
MIX-101 Mixing point of CO2 recycled
MIX-102 Mixing point of CO2 fed to process
MIX-103 Mixing point of CO2
MIX-104 Mixing point of treated water
P-100 Wastewater pump
T-100 Extraction tower
V-100 Degasser
V-101 Degasser
V-102 Degasser
V-103 Degasser
V-104 Degasser
V-105 Degasser
V-106 Degasser
VLV-100 Raffinate throttle
VLV-101 Treated acidic water throttle
VLV-102 Extract Throttle
VLV-103 Recycle CO2 throttle
VLV-104 Hydrocarbons throttle
VLV-105 Acidic water throttle